DEVELOPMENT
OF THE
COAL-TAR COLOUR INDUSTRY

BY

Dr. HEINRICH CARO, Ph.D.

Translated and Edited

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TO THE REVERED MEMORY
Of the late Professor
ANUKUL CHANDRA SIRCAR, M.A., Ph.D., F.N.I.
In Recognition of his valuable Contribution to the
CHEMISTRY OF SYNTHETIC DYES

FOREWORD

Mr. Sen and Dr. Biswas have approached me for writing a Foreword to their book, " The Development of the Coal-tar Colour Industry ". It is indeed not an original work. Nevertheless, its importance cannot be exaggerated, specially at a time when we are thinking of setting up a dyestuff industry in our country. I commend it to the students and research workers desirous of working in a dye-manufacturing work. The book should also be of great help to advanced students of Organic Chemistry.

Syama Prasad Mookerji

PREFACE

The reference of the present memoir was accidentally niet with while going through the life of Heinrich Caro in Bugge's well-known volume—*Das Buch der grossen Chemiker*. On perusal of the original article in the *Berichte* it was found to be a veritable spring of living inspiration and an inexhaustible store of information not only of the development of the chemistry of the artificial colouring matters but also of the development of the organic chemistry in general. What appears most fascinating is the vivid description of each and every side-line indispensable for the growth and expansion of a major industry. Caro himself being an embodiment of theory and practice—a great investigator in the field of dyestuff chemistry and at the same time one of the most successful founders and directors of many a flourishing dyestuff concern—is eminently fitted to give a first hand knowledge of the subject. Moreover, his intimate contact with most of the builders of the dyestuff chemistry and his close collaboration with some of the most distinguished savants in the line, have given him a unique opportunity to observe with keen interest the germination and growth of most of the sections of the synthetic dyes that have sprung up to splendid inflorescence during his own life time, towards the end of the nineteenth century. And this he has described in his inimitable lucid language, tinged here and there with the glow and ardour of his own personal reminiscences.

As India is on the threshold of industrialization, the eminent scientists, industrial magnets and politicians who are intent upon shaping the destiny of India's industrial future, will find in this memorable discourse of Caro a mariner's compass to put forth their energies in the right direction.

The history of the coal-tar colour industry is mainly the history of the two staple dyes, Alizarine and Indigo which were formerly of agricultural origin. Alizarine is the most valuable red dye of commerce, occurring in the form of a glycoside in the herbaceous perennial rubia tinctorium. The long, slender root of the plant when aged and ground furnishes Madder, the

source of the dye. The very name alizarine suggests that it was known to the Arabs and the Moors by whom it was introduced to Europe during the renaissance. The natural madder (garance) was an important article of French commerce for nearly two centuries and in the decade before the Franco-Prussian War its annual production was about 70,000 tons, valued at £4,000,000 and more than a third of a million acres of land were under its cultivation. This flourishing business was brought to a sudden collapse through the development of coal-tar colour industry by Hofmann's school. The immediate cause lay in the exhaustive chemical researches of Perkin, Graebe and Liebermann. In 1868 Graebe and Liebermann discovered that anthracene was the mother substance of alizarine and next year they (with Caro), and Perkin, independently took out patents for the manufacture of Alizarine from the coal-tar anthracene. Within ten years the natural product was completely ousted and the artificial Alizarine attained the highest peak of success. It is reported that from the manufacture of Alizarine, Badische Anilin und Sodafabrik made a profit of £1 million in the year 1881 alone.

The profits made by the German dye industry were not left idle. They were " ploughed back " into research on the production of synthetic Indigo. This commercial synthesis is based upon the classical investigations of Baeyer and the dogged determination of the Badische firm. After more than 25 years of ceaseless research the first synthesis of Indigo from coal-tar constituents was crowned with success. Soon a number of successful methods followed and in ten years the indigo acreage fell from 1½ million acres to a third and the export figures of India from £4,000,000 to a sixth. And in course of a few more decades the Indian plantation of Indigo almost completely vanished.

The artificial Alizarine and Indigo are the two land-marks in the history of coal-tar colour industry and the primary object of mentioning them here is to inculcate afresh to our students and industrialists the vast economic aspect of the dye industry and the great role which original research plays in the development of such a major national industry. Being intimately associated with these revolutionary discoveries Caro has furnished

in detail both the academic researches and industrial develop-
ments along with the discovery, isolation, purification and
economic production of the requisite coal-tar intermediates.
What proves an outstanding feature of Caro's speech is that
he gives a chronological development of all other branches of
dyes and chemicals with frequent quotation of original references
and dwelling unconsciously as it were on the general industrial
policy, training of personnel and the equipments necessary for
the successful running of a model dye firm. The merit of the
book is heightened by the inclusion of these indispensable data
which are seldom noticed in the ordinary text books.

To our aspiring students of higher chemistry the book will
prove a perennial source of inspiration as its pages will reveal
to them what an infinite patience and persevering work have
been spent on the foundation upon which stands in superb
grandeur the magnificent structure of our modern organic
chemistry. From its perusal the research students will acquire
a habit of critical study and a knack for attacking new problems.
The book is likely to be welcomed in other English speaking
countries too, by workers in the allied industrial fields, who in
the midst of the pressure of their professional activity can ill
afford to go through the original.

To meet any unkind remark against our endeavour at
unearthing this precious old piece, it is enough to aver that a
genuine gem can always stand the test of time. Just as the
age-old coloured glass panes in the windows of the ancient
cathedrals gain in brilliance as the years roll on, so the lapse of
years has added to the beauty of this work rather than diminished
its value a whit. To our awaking Indian nation at this point
of our industrial renaissance this memoir is of particular signi-
ficance in that at present we are most in need of high ideals
combined with a fund of factual knowledge and happily these
are to be found in overwhelming profusion in this memorable
contribution of Caro.

As it is folly to paint the lily even with the most brilliant
of our coal-tar colours, we refrain from re-touching the subject
matter altogether. Nevertheless it must be admitted that with
the limited knowledge of the language at our command we are
not sure if the spirit of the original has been retained all through.

However. no pains have been spared to make it as true a picture as possible, though here and there some peculiarly long sentences of old German even in their English garb may prove unfamiliar to those used to high-class English diction. But a modest hope may be safely entertained that absorbing interest of the subject matter will make the readers oblivious of such petty literary blemishes of the text.

To make the book useful and interesting to a larger circle of readers, biographical sketches of eminent founders of synthetic dyestuff chemistry together with their portraits have been inserted in different sections of the text and in the appendix a brief mention has been made of the later developments in the line. This historical account has been followed by the chapters on " Dyestuff Intermediates", " Important Dyes with their Compounds ", " Chemical Classification of Coal-tar Dyes ", " Classification of Dyes with their Relation to Textile Fibres ", and " Extra-Textile Use of Dyes ".

The appendix may, therefore, be treated as a worthy supplement to the very text itself and we are humbly of opinion that it has added considerably to the merit of the original discourse of Dr. Caro.

S. P. Sen,

H. G. Biswas.

CALCUTTA.
May.   1948

HEINRICH CARO (1834–1910)

HEINRICH CARO

1834—1910

Caro was born at Posen in Germany on the 13th February, 1834. His father as well as his grand-father conducted a big cereal firm. As a child Caro has seen the Adler dispensary in his paternal house at Posen and when a school-boy in Berlin, where his parents migrated in 1842, they had a chemist's shop in the house they lived. These early impressions made a profound influence on the future choice of his career. Chemical experiments with his friend Richard Peters and studies at the Berlin University and later at the Technical Institute (1852—55) followed, and laid the foundation of his future eminence. On leaving the University he joined in 1855 as an apprentice the dye and calico-printing works of Mülheim under the direction of the experienced colourist Achille Steinbach. In November 1859 he went to Manchester, the centre of the Cotton industry, for further training. Here fortunately he secured friendship of John Dale, chief of the Chemical Firm, Roberts Dale & Co. Caro started his career as an analytical assistant to John Dale on a modest initial honorarium of £1½ a week. He discharged his duty with great zeal. At the same time his attention was drawn to the magically enchanting rays of the newly discovered aniline dyes. At that time aniline was not a commercial commodity. Caro prepared it from Indigo and commenced oxidation experiments with it. Very soon jointly with Thomas Roberts and John Dale he began to erect his own factory. In running the factory he gained a great deal of practical experience. For, besides doing researches on new dyestuffs he had to look into the business side of the firm and had to design and supervise the constructional works himself. He made an improvement on the preparation of Perkin's 'Mauve'. In the London World Exhibition of 1862 his products were highly praised. He followed the works of A. W. Hofmann and his school with keen interest. Hofmann's works on Rosaniline, published on the 11th March, 1862, made a deep impression on his mind. He now felt a pressing necessity to make up his chemical studies for which he now began to burn mid-night oil. The sound scientific ground work which he had acquired in Germany now came to his assistance and filled him at the same time with a deep desire for grasping the intimate theoretical knowledge of the new groups of dyestuffs. In November 1862 Caro made personal acquaintance with Hofmann, who was then disseminating the German scientific knowledge at the Royal College of Chemistry, London. Here he also came in close touch with Martius and Griess who were working in Hofmann's laboratory. Caro also maintained a close touch with Adolph von Baeyer, Kekulé, Emil and Otto Fischer and as a result he succeeded in producing new and useful dyestuffs like Induline, Eosine and others. On the ground of health and also in consideration of the shifting of the centre of Science and technology from England to Germany with the home-return of Hofmann and Martius, Caro returned to Germany and settled at Heidelberg. Here he erected a small private laboratory and at the same time worked in Bunsen's

laboratory on his favourite subject of Rosolic Acid. Caro, however, was more an industrialist than an investigator and as such he could not remain contented with purely scientific research for a very long time. Under his inspiring influence very soon a number of chemical concerns began to grow up in the vicinity of Heidelberg—in Mannheim and Ludwigshafen. The most promising of these was Badische Anilin und Soda Fabrik, established on the 10th May, 1865 and the post of the Technical Director of which was offered to Caro on the 1st November, 1868 in recognition of his brilliant record of experiences in connection with such factories in England. The first year of Caro's joining the Badische firm had been of momentous significance especially as it synchronizes with the discovery of Alizarine. It is well known that Graebe and Liebermann who had discovered the synthesis of Alizarine from dibromo-anthraquinone at the end of 1868 handed over their discovery to Badische Anilin und Soda Fabrik for industrial exploitation. The starting material anthracene was still not easily available and the process also could not be carried out into industrial practice without difficulty—the handling of bromine being bothersome and expensive. Following an analogy of the conversion of benzene sulphonic acid into phenol by potash fusion, discovered in the previous year by Kekulé, Wurtz and Dusart, Anderson as well as Graebe and Liebermann tried this process in vain to obtain Alizarine. Caro, however, succeeded in this difficult job by raising the temperature of reaction. Thus the natural technical process for the manufacture of Alizarine was discovered ! At first the anthraquinone sulphonic acid was prepared in big glass flasks and the alkali fusion was conducted in silver kettles. Now the cast iron sulphonation vats and high-pressure fusion kettles were introduced. As a by-product of anthracene Caro discovered acridine. At intervals his attention was directed to the diazo compounds which led to the discovery of Palatine Orange from benzidine and nitrous acid in 1869. Since the beginning of 1870 he began the preparation of Induline from azo-benzene and its conversion into the induline-sulphonic acid. The month of June 1874 brought the publication of the second important discovery of Caro—the nitroso-dimethylaniline. In the meantime Caro was extremely busy with azo-dyes and in July 1877 he obtained the first red and valuable acid azo-dyestuff, the Fast Red.

In recognition of his brilliant researches in the field of synthetic dyes the University of Munich offered him the honorary, degree of doctorate in 1879.

Then commenced a further almost three years' lively contact between Baeyer and Caro or Badische Anilin und Soda Fabrik, in course of which Baeyer communicated his famous series of indigo-synthesis and to bring it into fruition the firm came forward with all possible means. For the technical utilization of the new synthesis Caro threw himself heart and soul to the work with his staff working indefatigably in the laboratory in an inspired state of mind in expectation of the momentous issue. It goes to the credit of Caro to prepare cinnamic acid from the cheap benzalchloride and sodium acetate at this time.

The correspondence that took place between Baeyer and Caro during this period reveals wealth of information to a student of chemistry and chemical technology. A letter dated the 15th June, 1878 written by Baeyer

to Caro describing his newly discovered satisfactory method of the conꞥ version of isatin to indigo blue with the help of ammonium sulphide is given below in the original.

Lieber Herr Doktor!

Endlich habe ich eine befriedigende Methode, Isatin in Indigblau überzuführen und zwar die Einfachste, die man sich denken kann: mit Schwefelammonium. Ich verwandle das Isatin mit PCl₅ in das Chlorid, wasche mit Wasser und träge das Ungelöste in wenigstens Schwefelammonium ein. Wenn alles gelöst, wird erwärmt, bis die Flüssigkeit dunkel wird, und dann mit Wasser versetzt und gekocht. Indigblau fällt sogleich in dichten blauen Flocken nieder, und zwar in Zustande grösser Reinheit. Ein prachtvoller Anblick für ein empfängliches Gemüt, wie wir es besitzen! Schwefelammon wirkt reducierend auf das CO, was Bedingung ist für die Indigbildung.

Herzlichen Gruss von Ihrem : A. Baeyer.

The fruitful period of the close collaboration between Baeyer and Caro reached practically its termination with the year 1883. It is found in Baeyer's letter to Caro written on the 28th August, 1883 :

" I have a mind to surprise you with a visit in October and to suck out from you once again the chemical ideas just as a bee sucks honey from the flower." But this wish of his was not realised as his line of work took a different course to purely scientific field (the study of ring-systems).

In the meantime Caro entered a new phase of activity in the domain of the Phosgene Dyes and the Auramine.

After retirement Caro erected a private laboratory in Mannheim and devoted the rest of his life to research work. Two well-known contributions came from this laboratory : The discovery of the rhodamines of the oxalic acid series obtained by the action of chloralhydrate on dimethyl-aminophenol, and permonosulphuric acid or Caro's reagent derived by the action of concentrated sulphuric acid on persulphate.

In his old age Caro loved the company of his old friends and colleagues as well as younger generations of chemists who frequently paid visit to his residence. He was never tired of relating the stories of his discoveries on such occasions which proved a source of inspiration to young listners. In his exuberance he often forgot the time for supper and it was only after repeated calls that he entered the dining hall with the guests at 10 or 11 in the night. Never did a visitor leave his house without getting some new light. The chemical literature of the time bears ample evidence of works stimulated by such visits to Caro. A mention may be made, for instance, of obtaining diphenylene glycollic acid from phenanthraquinone.

Even in the midst of his busy life Caro was always the true and loving father. He had 3 sons and 4 daughters and a number of grand-children among whom he passed the evening of his life peacefully and joyfully. He was a stranger to common-place social amusements. Home was his great centre of attraction and his harmonium brought him true recreation. After a brief illness Caro breathed his last in Dresden on the 11th September, 1910.

What made Caro an outstanding figure was the combination of a capacious memory, penetrating power of observation, sharp common sense and fundamental thinking capacity blended with a certain degree of artistic sense which are seldom found in one individual. He will continue to live in our memory as the most prominent of the founders of the coal-tar colour industry, as a man of quite extra-ordinary mental gifts and profound knowledge of patents, as an investigator imbued with the spirit of science, and as one who could call a rare series of outstanding discoveries and successes his own.

Though plunged in the distractions of business life and serene thinking of original investigations yet Caro found time for literary activity. Caro's contribution on the obituary of Peter Griess is a masterly specimen of his literary ability. But what stands as a landmark in the history of literature of the coal-tar colour industry is the discourse he delivered at the invitation of the German Chemical Society in Berlin on the 22nd June, 1891. This is an achievement of supreme order pervading as it does the patriotic satisfaction at the step by step development of the coal-tar colour industry by the contributions of his fore-runners, his contemporaries and his own, with infinite admiration for the founders of the science, especially of A. W. Hofmann and August Kekulé, and delineated in a style at once masterly and artistic with a fine touch of poetical fervour. A. Bernthsen has rightly remarked in the obituary of Caro that this memoir would prove a perennial source of inspiration and information to the coming generations of our students. An English version of this memorable work—"*Ueber die Entwickelung der Teerfarbenindustrie*"—forms the theme of the present volume.

THE DEVELOPMENT OF THE COAL-TAR COLOUR INDUSTRY

After we have gone through the comprehensive discourses delivered during the last few evenings on the recently developed domains of stereo-chemistry, synthesis of sugars and terpenes by the scientific investigators engaged in the lines, let us enter the field of activity of industry to-day.

Our path takes its course through the domain of coal-tar colour industry. This journey like the former cannot offer any charm of novelty. For, it is long since the chemistry of coal-tar has formed a regular branch of instruction and as such it occurs in excellent text books and annual reviews. Nevertheless, the known subject even creates ever a renewed interest whenever discussed. Indeed at this age of inventions chemistry has produced the most wonderful results in the field of colour industry Here the coal-tar, once an irksome by-product, but lo there its derivatives, a host of aromatic compounds with their numberless, daily increasing applications in science, arts and industry, indispensable helping agents to the chemical investigator, the physiologist, bacteriologist, the medical practitioner and serviceable also to the multifarious requirements of the art of dyeing, painting, photography and explosives! Besides the artificial dyestuffs, coal-tar derivatives are also the source of antipyretics, perfumes both of vegetable origin and of the musk, luxury, hundred times sweeter than cane sugar, and of explosives of devastating action.

The question always arises afresh—"How has all this come about? What further possibilities for expansion has it got?"

The course of development of the coal-tar colour industry gives us the answer. The movement started from the domain of dyestuffs. From the past we come to understand the present and to anticipate the future.

The local interest also influenced it. The industry which had originated in England and France—in spite of unfavourable

geographical conditions, remote from the source of raw materials and market of the products, greatly handicapped by custom barriers and foreign patent laws—found its principal seat in Germany after a severe struggle. No other branch of German industry bears with equal right the name of a 'National Industry.' We may ask: What causes led to this success? What must be done to keep it permanently to our soil?

> *The causes of German success have been repeatedly discussed by our English colleagues; compare specially: W. H. Perkin, J. Soc. Chem. Ind. 1885, 436; R. Meldola, J. Soc. Arts 1886, 759; Ivan Levinstein, J. Soc. Chem. Ind. 1886, 351.*

At this place however, every step in the domain of dyestuff industry awakens this evening lots of personal reminiscences. From here have emanated numerous valuable contributions on the investigation in that domain. Here was the first synthesis of a natural colouring matter jubilantly welcomed. With thankful reverence we look on the founder of the German Chemical Society, whose famous investigations on aniline have also at one time laid the foundation of the coal-tar colour industry.

But will our journey also satisfy the interest so highly aroused? Look at the lecture table and the elegance of its merry colours; specimens of all the derivatives of coal-tar produced in industry up to the time: their raw materials, intermediates and dyes, colouring on all sorts of textile fibres, represent kinds of application of the tar-derivatives in industries, arts and science. Structural formulae, models and diagrams illustrate the position of our theoretical knowledge.

Can we survey the whole field? Is it possible for a single picture with light and shade to put the combined investigations of science and industry mingled somewhat in a chaotic order, the work of more than three decades? And this also in the course of a single evening's lecture?

A task of such a nature would really be impossible now. Long past is the time when a Hofmann could satisfy his audience by lectures and experiments on the coal-tar colour industry—its

beginning from coal to the colouring matters. (*A. W. Hofmann, "On Mauve and Magenta", Chem. News* 6 (1862), 90.)   At that time people knew only Mauve and Magenta—at a far distance lay the theory.   Whoever since then might undertake to present the theoretical and practical details of the dyestuffs to his audience, could no longer force the multitude of facts into the frame of a single picture, even when surveying one particular field only. (*Cf. particularly: W. H. Perkin, "On the Aniline or Coal-tar Colours,"* 3 *discourses, J. Soc. Arts* 1869.   *W. H. Perkin, "The History of Alizarine and allied Colouring Matters,"* 2 *discourses, J. Soc. Arts* 1879).   Since the last of these discourses (*Ivan Levinstein, "The Development and present State of the Alizarine Industry",* 2 *discourses, J. Soc. Chem. Ind.* 1883, 213), an unforeseen amount of colouring matters and dye-intermediates have been prepared or have been known to be prepared, and there is scarcely a group of dye-stuffs whose constitution has not been brought to light.   Only from a series of lectures can this extensive field in all its various aspects be made known to a growing audience.

A survey of a particular section of the dye-stuffs only might probably be presented to us from this place in the course of time available to-day.   As such, a future sequence should form a valuable and complete survey of the whole work.   May then, what we hear to-day be the preface to what we expect to see before us, the coloured title page of that work.

By this the direction and aim of our to-day's path will be limited.   Its direction is the same which the development of the coal-tar colour industry has taken, its principal aim is the knowledge of the material, temporary and personal impulses which have decided this direction in the past and must continue to decide its legitimate rule in the future.   According to this plan we will begin our general excursion.

A guide offers his help to us.   He shows us the towering chimneys of an extensive factory.   *(A compilation of the individual firms together with the data of production, share capital, year of foundation, number of workers etc., may be had in the excellent Directory of Chemical industries of Germany by O. Wenzel.   A detailed description of the subject, particularly*

of the great work of G. Lunge may be had of: Die Industrie des Steinkohlenteers und Ammoniaks, 3rd Edition ; G. Schultz. Die Chemie· des Steinkohlenteers, 2nd Edition and P. Friedlander: Fortchritt der Teerfarbenfabrikation etc., may also be consulted. A concise and clear survey is contained in the work of Nietzki: Chemie der Organischen Farbstoffe, 1889, and of Julius: Künstl. Organ. Farbst. (Noelting 1887. Also consult: Tabellarische Uebersicht der künstl. Organ Farbstoffe by G. Schultz & P. Julius 2nd Edition).

"There", the guide says, "are the workshops of the German Coal Products Industry—I shall escort you to them. The factory includes all branches and accessory departments of this industry, and employs thousands of workmen, hundreds of chemists, engineers and tradesmen. Its machinery and output are most up to date. Its market is the world market. There you will find what you are looking for. The results and aim of coal-tar colour industry will manifest themselves before you more clearly in actual practice than in the books of the savants.

Amenities offered to the Workers :

On the way we walk through a long extended workers' colony. Hundreds of uniform, neat family quarters stand in series and cross series, surrounded by well laid out gardens, between them are built excellent-schools, club houses, common eating, washing and bathing establishments and shops of co-operative societies. Adjacent to it is the cottage-colony consisting of houses of the business managers and officers.

On the streets and parks is seen a healthy, merry-looking population—women and children. The men are in the factory. The whole sight presents a happy picture of order and care for the well-being of the workers. The guide tells us that the factory unceasingly adopts every approved method of safety. As a matter of fact every precaution is taken to minimise the dangers of the workers' profession, to protect them from accidents, to prevent and cure diseases and to provide for the proper recovery of the convalescents. They contribute generously to the insurance institutions for sickness and old age, take care for orphans and widows, for the veterans, invalids and victims of the

profession—all this, in collaboration with the State and the Trade Unions. The factory has taken a prominent part in the organisation of our new legislations on social progress. And all this come out gradually from the correct knowledge of the fundamental conditions corresponding to the development of the German industry. Not only the human sense of duty but also the well understood business interest requires well planned care for the growth, maintenance and elevating of a sound, contented and faithful working class, which forms the basis of prosperity of every industry. The manufacture of the tar products requires however, a specially reliable and well trained team of workers for the scrupulous prosecution of its subtle processes. For this purpose the German worker possesses a special knack. The elementary school has exercised its unmistakable influence on his intelligence, the compulsory military duty on his discipline. Military order prevails in the factory.

Now we stand at the factory gate, hesitating whether the fearful factory secret will forbid our entrance. Let us take a chance! With the familiar quotation (*A. W. Hofmann, Ber.* 10, 390). The time of the *Arkanisten* is over! We ask for admission.

The directors of the firm welcome us. We learn that now the industry does not rest on the pillars of the factory-secret as it did formerly. Under the regime of the German patent laws—to whose creation in 1887 the German Chemical Society (*Ber.* 2, 49; *Ber.* 10, 507), and to whose finishing in 1891 the Board of Dyestuff Industry had contributed successfully—the inventions of the chemists are appearing in ever increasing succession. To-day, he who considers patent laws unnecessary, runs the risk of his field of work being seized by his commercial opponents. With the present indispensable purity of products and the increasing refinement of their chemical and physical methods of investigation the secret of their origin becomes possible only in rarely exceptional cases. In numerous cases (*Eosine, Chrysoidine, Poirrier's Oranges, Fast Yellow, Light Green S, Primuline and others*) Hofmann's statement. (*Ber.* 10, 390) has come true: "He who in the last quarter of the 19th century will give a chemical problem to his colleagues, should be prepared that sooner or later

the problem will be solved." With the decline of the factory secret the dyestuff industry has gained an unthought-of blessing. Every published invention has fruitfully influenced the activity of all concerned, and has caused new inventions or improvements. The competition thereby rises to the maximum, the problem is investigated from all directions, the amount of experience is raised immeasurably ; the increase and improvement of the products, their price reduction and as a natural consequence the expansion of their applications are the result.

However, there are also—as in every industry—technical and commercial specialities which are excluded from the patent laws or whose nature is not impressed on the product. The *"Concurrence de'loyale"* the illegal competition tries to get hold of these specialities, unfortunately there is so far no protection against them though it has been sought for in collaboration with the colleagues. France is superior to us in this respect. Yet thereby the existence of the factory is not threatened any more as in former days.

Key to Success :

The reason for the continuous success of this industry which is still uninterruptedly developing, lies in the following: A practice saturated with knowledge to the last artery of the fabrication, permanent contact with the development of invention, the progress of theoretical and applied chemistry and the changing requirements of the market, a strictly maintained division of work and a systematically conducted harmonious co-operation of all hands, from the first to the last, every one put in his right place.

Above all : strength of character of the managers, of their business sense, diligence, sense of order and economy ; where, at any time, only one of these conditions was lacking, stagnation and retrogression were authentically sure to follow. The history of the coal-tar colour industry has proved the validity of this law at home and abroad.

This is the true 'factory secret.' A stroll through the workshop may show clearly the truth of the above statement.

We follow now our guide, and ascend a factory tower with him. From its top he says—"We shall recognize at a single glance the structure and the organic relationship, of the whole work."

We look down. A city.......... long lines of streets and squares. Every where railways for transport, wiring for electric light, telegraph and telephone. Out of the maze of big and small factory buildings, mighty buildings emerge. These contain, as we hear, offices of the technical and commercial management, the store rooms and laboratories for chemists and dyers. The picture is gradually dissolved into its constituent parts. At a distance we observe a river with landing-pier and ships, and the railway station with its goods trains. There the raw materials arrive. from where they are distributed through the main arteries, of the mighty body and from there the product ennobled by the art of the chemist goes to all parts of the world.

A Picture of Trade and Commerce :

Groups of big buildings stand out ever so much clearer now. A number of isolated works lie before us, stretching themselves in all directions like the big and small branches of a tree.

"There"—says the guide—"is the common stem. In that huge factory-complex recognisable by its high condensation towers and lead chambers, the inorganic chemistry prepares from a few minerals the most essential auxiliary chemicals for the tar-product industry. From the old stem the industrial branches of the organic chemistry have sprung up, and its growth has furthered their development. But a reaction has also set in. The demand of the dye-stuff industry has influenced to a considerable degree the increase of production and improvement of the heavy chemical industry and has led to the addition of new branches of manufacture. Already in the beginning, the preparation of nitrobenzene for the manufacture of aniline, called for a fast increasing demand for nitric and sulphuric acids. In quick succession numerous new applications for the nitrating mixture were found, and very soon one had to think of the utilization of the waste acid in the sulphuric acid plants. The Fuchsine led to the mass production of arsenic acid, which was

formerly prepared in small quantities only for the calico printing, and thereby led to a further expansion of nitric acid manufacture, and at the same time also to the regeneration of nitric acid from nitrous fumes and to the recovery of arsenic from the threatening heaps of Fuchsine residues. (*This technical problem has been successfully solved by A. Leonhardt in the factory of Gans & Co., Mainkur, 1877 Cf. D. R. P. 3216, but on account of the simultaneous displacement of the arsenic acid by the nitrobenzene-process it was too late, for a general acceptance*). ·

With the advent of sulphonic acid in industry, especially for Alizarine, Resorcin ,and Naphthol colour industry, new demand arose for the sulphuric acid manufacture. Not only an increased quantity of it but a stronger acid, from monohydrate to the anhydride were asked for.' There were improvements in the lead-chamber process and in the methods of concentration, and the mediæval process of preparation of Nordhausen Vitriol had to yield before the elegant synthesis of Clemens Winkler. (*Clemens Winkler* 1875. *Dingler's Journal* 218, 128). Through the anhydride now accessible, the progress in the domain of sulphonic acid, of the anthracene colouring matters and artificial Indigo was made possible, and thereby a new impetus was given to the manufacture of sulphuric acid and the obtaining of its basic material, sulphur dioxide from the waste gases of the pyrites and zinc blende. The demand for thionyl chloride also arose. A powerful impetus towards an increased production of the caustic soda was given by the alkali fusion of the anthra-quinone sulphonic acids and the application of the same method for the preparation of resorcin, naphthols and the numerous other ·products obtained by fusion methods. The competition between the Le Blanc and Solvay Soda Process and the prospective electrolytic method of the common salt supported the fusion process. With the introduction of the Ammonia-Soda process the alkali industry entered into a new phase of its development and geographical distribution. The then supremacy of England in this field was threatened and for its maintenance the perfec-tion of the then methods of production in a more scientific way was needed and a better utilization of the by-products, the soda sludge and hydrochloric acid, had to be sought for. The German heavy chemical industry also took an early part in this movement

and though hard pressed, provided the German dyestuff industry with an increasing supply of materials, which formerly were bought from abroad, and for which high taxes and freight had to be borne. (*The reduction of duty on soda ash from 4 marks to 1.5 marks in 1873 had brought the German Soda Industry in a distreesed condition*). And still more under an intelligent custom policy, (*Cf. Discussion on the tariff union bill, Chem. Ind. 1879, 150 ff. and debates of the Reichstag Chem. Ind. 1879, 266*) an ever increasing amount of soda, 4/5 of caustic soda produced from Ammonia-Soda process, even sulphuric and hydrochloric acids and bleaching powder became items of export in place of import. But the reaction of the English alkali industry had brought to life a mighty union of its factories (*United Alkali Company Limited, established in 1890 with a capital of £6,000,000, debenture £2,500,000, J. Soc. Ind. 1890, 1078. Hasenclever, Chem. Ind. 1891, 189*) and the success attained by the German industry can be put on a sure and permanent footing only by the incessant progress of the German technical science and of the transport organisation.

The influence of the dyestuff industry extends to other products of inorganic chemistry also. The chlorination of toluene, naphthalene, anthracene, the preparation of carbonyl chloride, the chlorides of phosphorus and other chlorinated compounds were added to the former applications of chlorine and led finally to the preparation of liquid chlorine in transportable condition. (*Knietsch Ann. d. Chem. 259, 100*). The fusion under pressure of Alizarine and the preparation of Aniline Black in fibres required the assistance of chlorates; the oxidation of anthracene to anthraquinone called forth the manufacture of sodium chromate to a great extent; Hofmann's Iodine Violet and Iodine Green raised the sale of iodine for the first time; the Eosine increased the demand of Stassfurt bromine and for the diazo and nitroso compounds sodium nitrite became a commercial commodity. |*In the factory of Roberts Dale & Co. in Manchester sodium nitrite has been first used since 1863 for the preparation of aminoazobenzene, Phenylene Brown and dinitronaphthol, and this sodium nitrite was obtained as a by-product in the preparation of arsenic acid by introducing nitrous fumes in caustic soda solution (E. P. 1858, No. 2242), principally employed in the pre-*

*paration of lake dyes for the oxidation of wood dye extracts.
Later big demand of the azodyes led to the independent prepara-
tion of pure, solid sodium nitrite by means of lead fusion method.]*
Lead peroxide proved to be a special oxidising agent for the leuco
compounds, and metallic sodium found application in the prepara-
tion of Antipyrine.   Liquid carbondioxide, sulphurdioxide and
ammonia became the usual reagents in the modern dyestuff
industry.   The dyeing of coal-tar colours led to the new com-
pounds of chromium, antimony, sulphocyanogen and fluorene as
mordants.

Out of the technique of inorganic chemistry, on which the
preparation of materials and industrial development of their
fabrication depend, the branches of the manufacture of organic
helping materials have also grown up, which are necessary for
the preparation and commercial application of the synthetic coal-
tar colour industry.   Mention may be made mainly of the pro-
ducts of the alcohol industry and of the dry distillation of wood:
Alcohols, alkylhalogens, ether, aldehydes, acetone and acetic acid.
Closely attached to them are glycerine of the fats, oxalic acid
obtained by the fusion of saw dust with alkali, further tartaric
and succinic acids, gallic acid from gallnuts and tannin—the
approved mordant for basic aniline dyes, the Turky Red oil
produced by the action of sulphuric acid on castor oil, and many
other products, amongst which—last but not least—the dextrine
used in commercial colouring matters for adjusting the position
of the types.   At the beginning of the industry alcohol and raw
wood spirit were the usual solvents for aniline dyes; soon some
were prepared in the better and cheaper dough form or one
strove with ever increasing success to replace spirit-soluble dyes
by water-soluble ones, but nevertheless methyl and ethyl alcohols
and to a lesser extent also amyl alcohol continued in time to
come to have an extensive and many sided applications, partly
directly as a solvent, a separating or alkylating agent, and partly
indirectly in the form of its active halogen alkyls, or as basic
material for the preparation of other alcoholic preparations.

Naturally therefore, a reaction on the alcohol industry also
was to set in.   The development of the methods for the prepara-
tion and estimation of pure acetone-free methyl alcohol, which

DEVELOPMENT OF THE COAL-TAR COLOUR INDUSTRY

we have at our disposal to-day, was principally induced by the requirements of the dimethyl aniline and methyl dyestuff preparations (*Ber.* 13, 1005, *Ber.* 7, 1492; *Ber.* 9, 1920). When Hofmann's Iodine Violet and Iodine Green were followed by Methyl Violet and Methyl Green, methyl iodide was replaced by methyl chloride. Methyl chloride was obtained in the liquid form from trimethylamine of the beet sugar molasses (*Vincent, 1877. Report of the World Exhibition in Paris in 1878 Von Ch. Lauth, 273 ff. In German Dye industry the liquid methyl chloride of Brigonnet and fils in St. Denis could not win a footing due to high transport and container cost*).

But one also turned to renewed investigations of the raw spirit and isolated the aldehyde, employed for Aldehyde Green from the first running of the distillation (*Ber.* 2, 401; 3, 75), and perfected the separation of the pure isobutyl and amyl alcohols. The latter then found applicaton in many extraction processes in place of ethyl ether specially when resorcin attained technical significance.

From the very beginning · acetic acid was an indispensable expedient. At first with its help the nitro compounds were reduced according to Bechamp's method, and in the preparation of English commercial Fuchsine, which at that time consisted of Rosaniline acetate, acetic acid was used and the same was the case with "Mauve-Paste."

Later an increasing demand arose for glacial acetic acid. It was first used as a solvent and diluent. With its help one prepared a number of acetyl compounds for the purpose of dyestuff industry as well as of therapy, and also a dye-stuff solvent glycerine acetate, "Acetine" for calico-printing. A promising field for application of acetic ester was found in the synthesis of Antipyrine. Sodium acetate became familiar with the still infant industry of substantive azodyes and with the development of the preparation of artificial Indigo the reciprocal action of dry sodium acetate and benzal chloride proved a cheaper source of the formerly used costly cinnamic acid. For the same purpose the demand of acetone arose and in recent times also the demand for chloracetic acid. Whatever will be the economically perfect solution of this technical problem the sister industries of the distillation of wood and coal, one of the living and the other of

the dead flora will always have to join hands for the development of 'this branch of industry. With the flowering of the coal-tar colour ·-industry powerful branches of its aromatic raw material have also developed, and we shall see their subsequent working in course of our further wandering. They are: Benzene, toluene, xylene, naphthalene, anthracene, phenol and cresol. How small appears this group in comparison to the series of hydrocarbons, bases and phenols which had already been discovered among the *distillation products of coal-tar and which, mixed with one another. are being used mainly for the less important purposes of heating and lighting only! Scarcely 1/12th of the weight of coal-tar, even about 1/5th of its oily distillate only consists of the products used by the dye-stuff industry *(On the field of end products Cf. Lunge, Industrie des Steinkohlenteers 3rd. Edn., 226 ff.).* And yet this small number in combination with a likewise limited choice from an immense store of inorganic and aliphatic compounds has brought about the abundance of its results achieved so far. The applicable combinations of these raw and helping materials have not been exhausted yet. However, one must not hesitate to find out new agents and to proceed on the path successfully covered by the scientific investigation of the heavy benzol, and the heavy oil *(Krämer & Spilker, Ber. 23).* *(Coumarone, indene, styrene, synthesis of chrysene, phenanthrene, anthracene and methyl anthracene. Schultze, Ann. d. Chem. 227, 143).* Sooner or later every new material will find its application. How long will naphthalene and anthracene remain as worthless substances!

"This short review"—concludes our guide—"shows already how closely the development of coal-tar industry is interwoven with its auxiliary industries. Mutual exchanging knowledge of the conditions of production, as well as of supply and demand must lead to new advancements. Then by further scientific rational work the German dyestuff industry will continue its present lead even when its up-to-date products and processes have become public property. But with Baeyer's words *(A. Baeyer, 'On the Chemical Synthesis"—Academic Address, Munich 1878, 522)*—"One discovery must lead to another and in this field Germany should never indulge in the tranquil exploitation of previous discoveries."

Another outwork stands next to the chemical auxiliary works. They are, as we learn, the mechanical workshops equipped with the most advanced machinery.   Machines and repair workshops, foundry, smithy, carpentry, workshops of the copper smiths, the lead solders, plumber, of the cooper, the carpenter and other workmen.   There the chemical apparatus are built, construction parts for the factories are prepared, boxes and barrels are made for the despatch of the finished goods.   All this is done under the direction of the mechanical engineers and the engineering architects who are assisted by a staff of draftsmen and constructors.   It is clear, therefore, that with such auxiliary means every new result of the laboratory can be put into process of the workshop without loss of time.

Initial Stage :

"Formerly in the first years of the industrial development" —says the guide—"it was quite different.   Almost everything had to be found by the chemist himself and he had to present sketches to the artisan ; the apparatus of the chemical industry of that time offered no model.   Everything had to be done in the way one prepared in the laboratory in flasks or beakers, under reflux condenser or pressure tubes, evaporated in porcelain or platinum basin, melted in silver kettle, fractionated with glass column or extracted in extraction apparatus and these often offered insurmountable difficulties for their transformation into the technical production.   In many cases one had to learn first of all the capacity for resisting of metals, enamels the earthen, stone and wooden vessels, against the attack of the chemical agents used during condensation and other operations and the corrosive action of the reagents was often raised considerably by pressure and high temperature.   One had to try the specific heating and cooling systems and had to invent mechanical stirring arrangement, filters, pumps and presses, drying and distintegrating apparatus.   A chemist who now-a-days joins a factory cannot, for example, imagine that the use of nitration and sulphonation in cast iron, potash fusion in cast and wrought iron kettles had to be invented.   He cannot also imagine that at first in many factories benzene was nitrated in glass or stone ware vessels :

that one prepared anthraquinone sulphonic acid in big glass flasks and melted its salts in a silver kettle. How different it is to-day! Only in rare cases do we require thoroughly novel arrangements. Almost for every operation of the chemist apparatus and machinery plans according to approved patterns are in readiness (*Sketches of apparatus and plans partly antiquated are to be found in the Works of Girard und de Laire*: *Traite des Derives de la Huille etc.*, 1873, *und Mühlhäuser*: *Die Technik der Rosanilinfarbstoffe*, 1889. *A complete technology of the dyestuff industry is still wanting*).

Present Stage :

The art of Engineering has taken them over and has perfected the often amateurish constructions of the chemical technologist to the highest mechanical efficiency—everything is more lasting, cheaper and more efficient than formerly. Special workshops for the demand of the dyestuff industry have been set up. Hand in hand with all that, the economical utilization of fuels, improvement of boilers, treatment of water, lighting, drainage and transport systems have developed. Dynamo, gas power and high pressure machines were added to the steam motors. Now-a-days one moves about in the well lighted, suitably and pleasantly laid-out well ventilated factory rooms provided with noiselessly working transport arrangements and one scarcely meets the time and space-killing filtering process of bygone days. It could not have satisfied the accelerated mass production of the present days. In its place the vacuum filter, centrifugal machine and even more the giant filter presses with their washing out equipments have come in. We can fractionate to any desired boiling point with the help of the fractionating column, distil heavy liquids in vacuum, sublime in air or steam, heat in autoclave, and melt in closed pressure vessels provided with stirring arrangements. Solid substances are disintegrated and powdered by disintegrator and ball mill, liquids are raised and stirred by steam jet blowers, which send the air under pressure up to a great distance. On demand high tension superheated steam, artificial ice, cooled air, hot and dry apparatus are ready for every purpose. Every where we see mechanics setting to work furthering and helping

the processes and the improvement secured by the application of new helping agents have influenced to a great extent the development the of coal-tar colour industry.

The success of the whole branches of manufacture is due to the introduction of suitable apparatus. In this respect the German machine technology also has achieved good success. The chemist has no longer to grasp at the construction boards, he can now concenrtate his attention on the chemical reactions in the manufacturing processes and it is sufficient when he can think in the same terms and speak as the building and machine engineers, who help him in his work."

"And is it for that purpose"—we ask—"the training at the institute of technology indispensable?" •

"One distinguishes at present"—so runs the answer—"between the laboratory and the factory chemists. The former devises processes and states their scientific conditions, the latter puts them into practice, supervises and improves their daily operation. Both kinds of profession are seldom exercised jointly now-a-days.

Training of a Chemist :

A theoretical training which embraces the entire chemical field continuing up to the independent solution of chemical problems is the fundamental condition for success in the later life of both categories of chemists, in particular of the industrial chemist, who loses easily the contact with pure science due to his devotion to professional duties. This training may be acquired at the University or at the Engineering College (Technical High School). It depends on the teacher and on his personal example whether the chemist trained under him would become a research worker. Also the general knowledge of applied chemistry and its working and methods of investigation which are necessary, for every body, can be obtained at both the institutions. However, the factory chemist if he does not want to remain a one sided *Autodidakt* (self-taught) in his future practice, considering the ever increasing divisions of work—needs moreover a training in mechanics, which up to now is offered by Technical High Schools only. (*Compare the confirmation of*

these remarks in W. H. Perkin's 'Presidential Address' London Chem. Soc. 1884, 223. Further Henry E. Armstrong, British Association, Aberdeen 1895, Address to Chemical Section). It is a general experience that the University scholars who had been specially gifted, have nevertheless practically become prominent factory managers in the coal-tar colour industry. Yet these are exceptions with which to count in advance is difficult. Therefore, as a rule, one gives perference to a chemist who has previous scientific as well as technical training when appointing him in a factory.

We look round further. Now we clearly distinguish a large central group of workshops from which long extended lines of buildings branch off in four cardinal directions.

Three of them—we are told—are alloted to the preparation of the three principal groups of the coal-tar dyes. The first, distinguished as the oldest of the buildings, serves for the manufacture of aniline dyes, which began in 1857 in England, and in 1859 in Germany, particularly of Fuchsine and its violet, blue and green derivatives and related compounds, further of the resorcin dyestuffs, the Safranine and Induline, the Methylene Blue, the Auramine and Rhodamine and of others, mostly basic dyestuffs and their sulphonic acids. This is principally the domain of benzene and its derivatives. The second series of workshops whose construction began in 1869 shelters the industry of artificial Alizarine. There the madder dye-stuffs are produced, their derivatives and analogues, as well as others, in combination with these or similarly applicable mordant dyestuffs, as Baeyer's Galleine and Coeruleine, the Naphthazarine of Roussin, the Galloflavine and the Alizarine Yellow. Anthracene particularly finds its application here.

The third group of buildings with their shining reddish roofs of dye dusts is the youngest. With the exception of the building for Phenylene Brown, which was established in 1864 and expanded with the appearance of Chrysoidin, this big complex dates from the year 1877. There the azo-dyestuffs and specially naphthol dyes are manufactured. In the extensive new buildings of this group the substantive azo-dyes which dye cotton fabrics without any mordant are prepared since 1884. This is the principal region of naphthalene.

In the fourth direction the buildings 'for the ma iufacture of modern antiseptics, antineuralgetics and antipyretic medicaments are laid out. They branch off from the store house of carbolic acid which at first was used with such a remarkable success. In the building where recently experimental preparation of quinoline as well as oxyquinoline of Skraup (*Wiener Monatshefte* 1882, 531, *D. R.-P.* 1881, *No.* 14976) and its active alkylated hydroderivatives Kairolin and Kairins (*O. Fischer Ber.* 16, 719 *Hofmann & Königs, Ber.* 16, 739) had been carried out and where in 1884 Knorr's antipyrine had been synthesized, is to be seen. (*Knorr, Ber.* 17 2037; *D. R. P.* 1883 *No.* 26429). Further more one prepares there thallin (*Skraup, Wiener Monatshefte* 1885, *D. R. P.* 1884 *No.* 30426), the acetanilide or antifebrine which is credited to be endowed with un .... properties, phenacetine (*Hinsberg u. Kast, Ber.* 20, 730 *Ref.*), further salicylic acid derivative, salol (*Nencki D. R. P.* 1886 *No.* 38973), inodorous substitutes of iodoform and series of other medicaments mostly still in the stage of clinical experiments, amongst which are included also the antiseptic Pyoctanin dyes (*Stilling, Anilinfarbstoffe als Antiseptika, Strassburg* 1890) and the hunger stimulating orexin (*Paal und Busch, Ber.* 22, 2685, *D. R. P. No.* 51712).

The great central group, however, from which these four different groups of factories have branched off in four different directions is at the same time also the most important one so to speak : the heart of the factories. From the distillates of coal-tar, in conjunction with the materials of the auxiliary industries and the synthetic methods developed by science and practice, innumerable intermediate products are prepared there. These are then consumed by those four arteries, where they undergo the process of oxidation, reduction, condensation of manifold kinds to convert them eventually into the final and commercial products. The buildings at the end of this group contain the store rooms of the raw materials, which come from the indigenous and foreign tar distillation plants and the refining works where necessary refining is made of the commercial benzene and anthracene. Phenol, cresol and naphthalene of any desired degree of purity can now-a-days be purchased from the German tar works.

2

Far away from us and half hidden behind explosive-protecting earthwork walls a group of low-roofed factory buildings are pointed out to us. There explosives are manufactured: Nitro-compounds of all types, particularly picric acid and the melinit (*Sir Fred. Abel, Chem. News* 61, 148. '*Prometheus*' Von O. N. Witt, 1892, 209).

At a still further distance we·see the imposing factory of Fahlberg's saccharine and as the last fragrant flower of the industry stands the isolated factory of Baur's artificial musk [*Fahlberg und List, Benzoesäuresulfinid, D. R. P.* 1884, No. 35211; *vergl. Stützer: Das Fahlberg'sche Saccharin (Vieweg* 1890) *und Fahlberg, J. Soc. Chem. Ind.* 1887, 587. *Baur, Trinitroisobutyltoluol, D. R. P.* 1888 *No.* 47599].

Getting acquainted with the precinct we now resolve to have a casual glance at the domain of raw and intermediate products and their coloured derivatives.

Benzene—its Source, Output and future Prospect :

At the entrance of the benzene store house we see a tablet with the inscription:

|		
A. W. v. Hofmann.	..	.. 1845
August Kekule.	..	.. 1865

"What is the meaning of this?"—we ask.

"It is in memory of the discovery of benzene in the coal-tar distillates by Hofmann, and of the establishment of the *Benzene Theory* by Kekule."

"But benzene had already been known for a very long time."

"Certainly. However its discovery in the oils separated in the compressed illuminating gas by Faraday and further its preparation from benzoic acid by Mitscherlich and Peligot have been merely of scientific interest. It was only with Hofmann's conversion of coal-tar benzene into aniline that the attention of the industry was turned towards it as a source of coal-tar dyes " (*Hofmann, Ann. d. Chem.* 55, 201).

"And is this source inexhaustible? Is it not menaced by the introduction of electric light?" "We entertain no such fear"
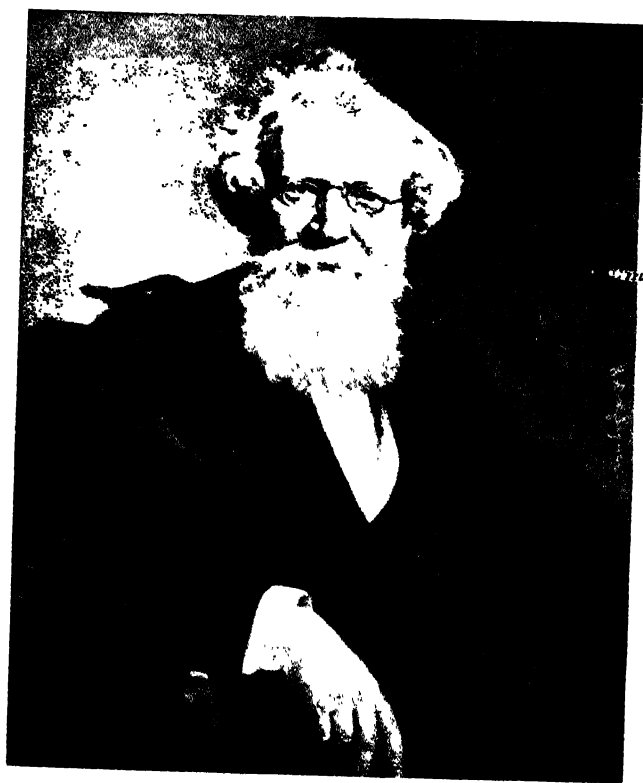
A. W. A. HOFMANN (1818–1892)

AUGUST WILHELM VON HOFMANN
1818—1892

Hofmann was born on the 8th April, 1818 at Giessen where he grew up ·in the scient fic atmosphere of the small Lahn-University. His father, an architect, was a man of earnest endeavours and he possessed a great love for what was good and noble. Hofmann imbibed these traits of his character at an early age. The father had also a hobby for travels and once he made a journey with his boy to Italy and France and this kindled in young Hofmann an unconquerable inspiration for•the beauty of art and Nature.

In the autumn of 1836 Hofmann joined the University of his native ·town to study law but he also attended the•lectures of mathematics and natural philosophy and he was particularly attracted by अ'ाॅ.ढ़़.ॉॉॅ.ॅ.ॅ' analytical chemistry conducted by Liebig. •Little Wilhelm soon became a favourite disciple of the great master. It was a remarkable chance that Hofmann undertook his first independent work with that substance, *viz.,* aniline, a coal-tar base which later established his great reputation. For, unexpected power of transformation of this substance in his hand proved the starting point for the modern dyestuff industry. In 1841 he obtained his doctorate degree with *Summa cum laude.* Two years later this work, *Chemische Untersuchung der Organischen Basen in Steinkohlenteer* appeared in Liebig's Annalen.

A former student of Liebig, Ernst Sell had built a tar distillation plant at Offenbach a. M. and from this factory Hofmann obtained two pounds of base from 1200 pounds of tar oil. In 1826 Otto Unverdorben, a Berlin Chemist, discovered an oily organic base by the distillation of indigo to which the name Aniline had been given. In 1845 Hofmann prepared· aniline by the reduction of nitrobenzene, obtained•by the nitration of benzene, which had up to that time been derived solely from gum benzoin. It went to the credit of Hofmann that he now discovered that the principal constituent of the light boiling part of the coal-tar consisted of benzene and he proved the identity of the coal-tar aniline with that of Unverdorben. In 1845, when the Royal College of Chemistry, London, was ·founded, Hofmann was invited to take charge of this institution. Under his inspiration the study of practical chemistry in England made extraordinary progress. He discovered the method of vapour density determination under reduced pressure. With Muspratt he discovered paratoluidine and nitraniline. His work on amines, ammonium and phosphonium compounds and on dyestuff is regarded as classical. It has rightly been stated that the cradle of coal-tar colour industry lay in Hofmann's laboratory. His personality, his inspiring lectures and towering genius attracted gifted and zealous students around him. Among those who came to lime-light in later years mention may be made of—W. H. Perkin, Sir Frederick Abel, Warren de la Rue, E. C. Nicholson, Ch. Mansfield, Sir William Crookes, J. Stenhouse, Peter Griess, Georg Merck, C. A. Martius and J. Volhard.

The great influence of Hofmann on industrial development was made manifest by the unparalleled triumph of the coal-tar colours exhibited at the London World Exhibition of 1862.

German men of science including Liebig now expressed a fervent desire that the master should no longer remain in a foreign land. And in May, 1865 Hofmann returned to Berlin where according to his plan a big laboratory with beautiful auditorium was built in the George Street connected with the spacious private laboratory with dwelling house in the Dorothee Street. The very first activity of Hofmann was to establish the Germann Chemical Society in 1867. He was the soul of this society as is evident by the fact that in 23 years 14 times he adorned the office of the president.

Hofmann's return to Germany was a great loss to England which has been expressed by the great English scientist Sir William Ramsay in 1903 when he was presented with the Hofmann gold medal by the German Chemical Society. He said,—" We all know the loss sustained by England through Hofmann's return to Germany. And I express the feeling of all English men of science when I say that had we retained him in our midst the great development of German chemical industry would have remained suspended and England would have attained the foremost position which Germany now possesses."

Hofmann was held in high esteem in all the scientific circles. He acted as a jury in the World Exhibitions. His merit was recognized in Paris in 1867 by offering him the Grand Prize of 1000,000 Frcs., and the French Government nominated him to the Officer of the Legion of Honour. Since 1847 Hofmann became the foreign secretary of the London Chemical Society and he was elected its President in 1861. His 70th birth day was celebrated by the German Chemical Society with great pomp when they established the "Hofmann Foundation". His friends and admirers presented him with a beautiful marble bust made by the famous sculptor Schapers on this memorable occasion.

Full of physical and mental powers the indefatigable investigator sank to his last sleep on the 5th May, 1892.

To perpetuate his memory the grateful German nation according to the design of Otto Marchs erected the 'Hofmann-House', which was completed in 1900. But the most beautiful and lasting monument had been erected by Hofmann himself in the hearts of his innumerable students, in the Annalen of Science, and in the German Chemical Society, where his name and his spirit will act as an inexhaustible source of inspiration.

—was the answer. "Indeed up to now the main source of ,our products is still the coal-tar of the illuminating-gas works. But its production in its steady increase was as little checked by bulbs and arc lamps as it was formerly by paraffin oil and petroleum (*Wright, J. Soc. Chem. Ind.* 1888, 542). On the contrary, the ever increasing- demand for light has resulted in a greater consumption of gas with consequent increase and improvement of gas burners in gas consuming and regenerative lamps and invert burners. Meanwhile gas production had to keep pace with the growth of cities and factories. The use of illuminating gas ,has increased for heating purposes and for gas motors. Water gas has not yet challenged it. At any rate, however, we have at our disposal a great reservoir, a part of which only has been utilized."

"And where are these reserves? "

"For the most part in coke oven works. [*Besides Lunge's 'Coal-Tar' Cf. specially Lürmann: Stahl und Eisen* 1892, 186; *Hüssener, do.* 1883, 397; *Otto, do.* 1884 *No. 7. According to Lürmann there were in Germany at the beginning of* 1892, 15726 *coke ovens with an annual production of about* 7¾ *million tons of coke in the factory and of that not even* 10% *were provided with arrangements for by-product recovery. The most widely used 'Hofmann Otto-Oven' produced according to the nature of coal— from a ton of dry coal* 680—760 *kg. coke,* 27.5⫶42.8 *kg. tar, and* 8.5—12 *kg. of ammonium sulphate*]. The preparation of a solid coke for furnace purposes, while obtaining at the same time a gas-tar equal in rank to coal-tar and of the ammonia indispensable to agriculture, to Ammonia Soda industry and to other chemical industries, as well as of combustible gases, can after long years of experiments the problems be considered solved technically. In the place of the primitive, open coke ovens with their flames glowing red at night in which the valuable tar-distillates were uselessly burnt, an increasing number of closed distillation ovens have been introduced. The bottom and side walls of these new ovens are raised to as high a temperature as possible according to the regenerative principle of Siemens, by the gases returned to the condensation of the tar together with the admission of heated air. (*Due to its cheap contrivance and good working*

efficiency⟩ *the recently introduced* **Semet-Solvay** *Oven requires no regeneration system*). For, only the coke oven tar produced at high temperature contains the aromatic compounds of gas-tar; from other systems of oven without external heating and with colder gang way and partial internal combustion just as out of gases from blast furnace run with coal, so out of generator gases, an excessive amount of paraffins and lower hydrogenated tars, similar to the brown coal-tar and mostly of useless type are obtained. (*Watson Smith, J. Soc. Chem. Ind.* 1883, 495; 1885, 451; 1887, 583. *Lunge und Schmid, Chem. Ind.* 1887, 337; *Lunge, J. Soc. Chem. Ind.* 1887, 580). ⸱The general introduction of this coal distillation, which in range would far surpass the gassing of coal in illuminating gas works is hampered by the high establishment costs of ovens and condensation apparatus as well as by the extraordinarily fluctuating price of the gas-tar products. However, with business foresight the progress of tar and ammonia production of the coke ovens has been completed irresistibly. No lack of tar is to be feared any longer.

A further source of benzene is the gas itself. The illuminating gas owes, as is well known, a considerable part of its illuminating power to benzene and its next homologues, present in the gas. The benzene content of the gas is estimated to be more than twenty times the yield of benzene from the corresponding quantity of tar. Already in 1863 John Leigh tried to recover it in the form of nitrobenzene for the purpose of aniline dyes. In the City Gas Works of Salford, near Manchester, he passed the gas through strong nitric acid and obtained from every 10,000 c. ft. of gas—the product of 1 ton of canal coal—one gallon of benzene in the nitrated form which was 16 times the amount from the corresponding quantity of tar obtainable at that time. (*The then annual gas production of Manchester amounted to* 800 *million cubic feet. John Leigh calculated that the possible benzene production of Manchester alone was* 80,000 *gallons annually. Letter communication of the 4th April* 1863. *Irwin* (*J. Soc. Chem. Ind.* 1887, 93) *estimated later that the benzene content of* 10,000 *cubic feet of Manchester gas as being* 3 *gallons. Compare also Davies, J. Soc. Chem. Ind.* 1883, 815 *and John Leigh, Engl. Pat.* 1863, *No.* 44). As for the separation of benzene, John Leigh however, did not strike the right path, ⸱the

nitrobenzene was impure and the gas could not be/used for illuminating purposes. Only an artificial price raising of benzene during the winter of 1868 led again to the resumption of these expriments and through an accident—to the observation, that benzene could be fully extracted from the illuminating gas by an indifferent solvent after which it could be separated from the solution by distillation. The disclosure of this fact [*Engl. Pat.* 1869, No. 488, *"An improved Method of obtaining Benzole and its Homologous Substances from Coal gas", W. R. Lake (H. Caro, A and C Clemm, F. Engelhorn). The large scale experiments in the city gas works of Mannheim conducted with heavy benzene as the washing agent,. produced no decrease of the illuminating power of the gas. The gas after delivery of its benzene etc.* (18-20% *of absorbents can be distilled. from it under* 130°) *was again carburated at the cost of heavy benzene* (b. p. 130-160°). *Meunier has been erroneously credited with this process* (*J. Soc. Chem. Ind.* 1883, 500 *Cf. Irwin, Soc. Chem. Ind.* 1887, 93; *Levinstein, do.* 1883, 217] had resulted in the exploding of the commercial 'benzene clique' but thereby also the technical requirements ceased for the time being for further experiments. 'The washing of benzene-containing gases' got practical significance only in recent years, when the recovery of coal-tar ammonia in coke oven works became more and more practised. Now people began also to wash the coke oven gas before its burning with heavy oil (*Simon-Carvé, Engl. Pat.* 1884, *No.* 15920) and obtained in this way, specially in Germany, huge quantities of benzene. However, the profitability of the requisite plants, is naturally dependent on the market price of the gas-tar benzene. (*A market price of 2sh. 6d. per gallon is considered the lowest profitability limit in Germany. Chem. Ind.* 1892, 147). In any case, this new source in combination with the increasing production of coke oven tar acts as a safety valve against renewed attempts at the artificial price-raising. *Over production of our important raw materials is much more to be feared than lack of them.* At the same time the German industry will evidently become more independent of foreign import. (*Benzene from the total German coke oven factories can cover the indigenous requirement at present. Chem. Ind.* 1892, 147. *Up to now the import of light oil does not show any considerable decrease. This*

is explained by the increase in consumption).   However, this consideration does not exhaust all the precautions for further reserves although in this state of affairs their demand seems to be postponed for an indefinite period at least in Germany.   Already years ago experiments on small and large scales have shown the possibility   for   obtaining   benzene   hydrocarbons,   poorer   in hydrogen, as well as naphthalene and anthracene in enormous quantities from high boiling brown coal-tar oils, particularly also from Caucasian petroleum residues by the method of super heating, (*Cf. Liebermann and Krämer, Treatise on the Union of industry* 1882).   However, as has been stated, the necessity for the utilization of these experiments must remain reserved for the future.   (*According to a friendly private communication of Hugo Erdmann, this question occupied people again at the time of his stay in Baku (Spring 1891). An experimental factory is said to have been erected there by Rothschild*).

The carbonisation of the low grade coal or coal wastes became current in England not in smelting factories but in retort works (*Hardmann, Engl. Pat.* 1882, *No.* 4312; *Davies, J. Soc. Chem. Ind.* 1883, 522. *The management of these carbonisation works is profitable now only in the hands of the coal-mine owners.. In the previous year* 354000 *gallons of* 90% *benzene were produced. From coal dust at* 10d. *per ton* $1\frac{1}{4}$ *gallon was obtained without cooling and* $2\frac{1}{4}$ *gallons with cooling during the absorption. Friendly private communication of Mr. George E. Davis*) and in the vicinity of collieries with the principal object of obtaining tar, ammonia and benzene with the best possible utilization of by-products, coke-residue and washed gases might with regard to the increasing development of the coke oven industry and of the retarding price of benzene be looked at as a further reserve only for an improbable emergency. The initially expected expansion was not attained by this industry. On our enquiry for the present range of benzene production we understand that in 1890 England and Scotland produced about 2/3 of the total quantity. By degassing 10 million tons of coal in the big gas works of these countries about 500,000 tons of gas-tar were produced—5 times the annual production of Germany of which, however, 93-95% only have been distilled. The remaining gas-tar was either burnt under the retorts or was used for

other purposes such as a paint and preparation of tar-board etc. The production of commercial benzene and toluene from gas-tar by taking an average yield of 1.5%, is estimated to be about $7\frac{1}{2}$ million kg. for England, $1\frac{1}{2}$ million kg. for Germany and the same quantity for France, Belgium, Holland and Austria. To this was added over 1 million kg. from English carbonisation works and already about 2 million kg. from the German coking or 'coal distillations' so that total German production from gas-tar and coke oven works was in fact raised to about $3\frac{1}{2}$ million kg. or to over $\frac{1}{4}$ of the total production and to 4/10 of the English production. Germany has, therefore, still to depend on England. In 1890 the import was estimated to be over $7\frac{1}{2}$ million kg. to the value of $6\frac{1}{2}$ million marks but this situation was gradually to change by the continual production of benzene from the German coking concerns. We hear that of the total business value of the intermediates, dyestuffs and medicaments etc. derived from coal distillates even an approximate estimation is lacking. The import and export statistics—production and consumption of the various countries do not offer a sufficient clue. The consumption of the producing countries is not ascertained. The export and import figures are calculated on the basis of estimated values of different forms of weights, of dry, moist, pure and mixed products. One can suppose that the total value comes to about 90-100 million marks of which 2/3 holds the German production. Switzerland occupies the next position, then come England and France.

Refining Department :

On entering the refining department of raw commercial benzene we notice a long series of powerful column apparatus of Savalle, with which we are well acquainted in connection with spirit distillation (*Sketches of Savalle's apparatus, Cf. Bolley's Technologie (Rich. Meyr), V. 4 Pp.* 541).

The guide remarks that the separation of benzene and its homologues depends also, as the rectification of crude spirit, on the principle of dephlegmation. Hofmann's highly gifted pupil, Charles Mansfield (*Mansfield, Chem. Soc. Quart. Journ.* 1,244 (1848) ; *Ann. d. Chem.* 69, 162; *Hofmann, Ber.* 4, 162. *Sketches*

of the apparatus of Mansfield: *See Roscoe-Schorlemmer, Hand-book IV, 59. On Mansifield's results of Warren, Chem. News.*
12, 279 *and 97, remarks*), inspired by his teacher first undertook the systematic separation of light coal-tar naphtha according to this principle which he had already applied and to him we owe the first exact knowledge of the coal-tar constituents. He was also the first to design the spirit apparatus. But in the earliest period of the aniline dye industry his results remained mostly unnoticed. The aniline factories were supplied with imperfectly purified benzene of indefinite boiling point-ranges—some preferred the high boiling benzene, others the low boiling benzene for the French or the English aniline. Although one found considerable differences in the yield and quality of dyes derived from such sources, in practice the real cause of it remained hidden. There was no end of empirical testing and conjecture. Suddenly science helped to clear the matter. A surprising discovery showed the technique which had already been adopted by Mansfield.

On our enquiry about this discovery we hear: In June 1863 Hofmann found in the course of an investigation on the isomerism of the phenylenediamine discovered by him (*Hofmann, Proc. Roy. Soc.* (1863), 12, 639) that perfectly pure aniline prepared either from isatin, benzoic acid benzene or pure coal-tar benzene could not be oxidised to Aniline Red. (*Hofmann, Proc. Roy Soc. (2nd June* 1863) 12, 645).

For the solution of this problem science and practice joined hands. It was one of their earliest alliances. Edward Chambers Nicholson, the chief of the then well reputed London dye firm of Simpson, Maule & Nicholson, a former student and assistant of Hofmann, had in an empirical way already forwarded the opinion that aniline was not at all the active agent for the formation of Aniline Red. At once he sent a gallon of pure aniline from coal-tar benzene boiling constantly at 182°C to his professor. It gave in fact no Aniline Red. In addition there were lots of commercial aniline boiling from 180-220°C. From these Aniline Red could be produced in rich yield and Hofmann concluded that apparently commercial aniline contained a different base from the normal aniline whose joint action seemed to be indispensable for the formation of Aniline Red. "Which was then this base?"

Characteristic of the opinion of that age—shortly after Kekule's benzene theory had been initiated, the investigator had the following train of ideas: "Is this base perhaps some isomer of aniline, some derivative of the benzene isomer, the parabenzene of Church? Or is it a base analogous or homologous to aniline?" For the first time we see here, in the dyestuff industry the questions of homology, analogy and isomerism, later on so significantly coming to the fore ground of practical interest. The scrupulous separation of this puzzling base on a small scale from the commercial aniline or similar methodical separation of the hydrocarbons from which this base-mixture is derived has been reported by Hofmann in his memorable article (*Hofmann, Proc.* *Roy. Soc. (9th June,* 1863) 12, 647). He, therefore, tried the synthetic experiment. Under his hands the results of his previous theoretical investigations came to life. Fortunately he possessed some specimens of the homologues of aniline. Their presence in commercial aniline could scarcely be doubted, as already Nicholson had claimed toluidine to be the true source of Aniline Red. Hofmann remarked in his first communication (*loc. cit.* 646) that sometimes practice is far ahead of theory. So the first thing to be tried was solid toluidine obtained some 18 years ago from tolubalsam in collaboration with Muspratt (*Muspratt und Hofmann, Ann. d. Chem.* (1845), 54, 1). Again a new problem! This also produced no Aniline Red, but now the darkness was illumined by a lucky experiment. A mixture of pure aniline and toluidine when heated with zinc chloride, mercuric chloride or arsenic acid gave rise in every instance to a magnificent red of intense dyeing property—our Pararosaniline of to-day! From the commercial aniline a considerable portion of toluidine can in fact be separated. This surprising observation, however, received its full significance first by its connection with the formula of Rosaniline $C_{20}H_{19}N_3,H_2O$, which Hofmann, had established a year ago (*Hofmann, Proc. Roy. Soc.* 12 (20th *Feb.* 1862), 6). Uptil then uncleared 20 carbon atoms now received their first systematic significance. They dissolved into the sum, 6 plus 14, 1 molecule of benzene and 2 molecules of toluene. Thereby the industry not only got hold of the genesis of Aniline Red but what was still more important that the way to the rational utilization of benzene and its homologues for all present

and future manufacture of dyestuffs was cleared. First of all
one had to fractionate the raw materials and the significance of
these individual constituents and their mixtures had to be ascer-
tained by experiments according to fixed molecular ratio for
every given case. From such experiments one could expect to
get an idea of the working of the commercial raw materials.
There was also the prospect to foresee that in this way uniform
colouring matters of fixed properties could be secured. Such
colouring matters were supposed to offer a sure support for the
analysis and determination of constitution. Starting from pure
materials and keeping in view the aim of an individual dyestuff
of exactly known formula, one finally could think of drawing
equations   for   synthetic   compounds. Thereby   the   crude
empiricism had to turn to methodical work, illuminated by science.

Again one fell back upon the investigations of Mansfield, to
which the life of this youthful pioneer had been sacrificed. (*The
benzene burn through which Mansfield succumbed* (1856), *took
place in his private laboratory in London and not in the College
of Chemistry. Hofmann had found bigger experiments too
dangerous there. Hofmann's private communication*). The
industry also has its martyrs! Shortly before Hofmann's publica-
tion Cupier had undertaken (*Jean Theodore Coupier, Fr. Brevet
No.* 58085 *of 4th April* 1863. *The apparatus described therein
shows combination of a steam distillation vessel with rectification
columns and a system of reflux condenser with baths for constant
temperature. In 1868 Coupier's incomplete apparatus first found
experimental application in Germany*) the systematic separation
of benzene and its homologues on a large scale for the preparation
of pure hydrocarbons and their pure derivatives, particularly
pure aniline and pure toluidine for use in the dyestuff industry.
But only by the new insight into the process of formation of
Aniline Red a stimulus for the requirement of individual materials
for experiment appeared. In every factory one began now to
fractionate and separate coal-tar constituents, one determined the
actual boiling point ranges of those mixtures which had proved
suitable, fell back to the tar distillers and aniline manufacturers
and asked them to stick to fixed prescriptions. Stricter than
before notion was fixed on the 30, 50 and 90 benzene, from which
30, 50 or 90 volume per cent. distilled up to 100°C from a test

distillation.   From almost immediately following but not less surprising elucidation of Hofmann on the nature and process of the formation of Aniline Blue (*Hofmann, Proc. Roy. Soc.* (1863), 13, 9) and Toluidine Blue (*Hofmann, Proc. Roy. Soc.* (1864), 13, 435) one became aware of the significance of pure aniline for phenylating the Rosaniline and one distinguished clearly between the 'aniline for blue' and the 'aniline for red.'

Although the unseparated mixtures of the old directions for use particularly for Fuchsine were maintained still for some time to come, yet the demand for pure benzene, toluene and finally xylene increased with the increasing number of synthetic dyestuffs.   Whilst the first became the clearly known basis of the numerous synthesis with dimethylaniline and its nitro-derivatives, for the manufacture of resorcin, of diphenylamine, of benzidine, for the production of Induline and other dyestuffs, pure toluene was wanted for the synthetic application of benzyl and benzalchloride, benzaldehyde and benzotrichloride, for the preparation of ntrotoluene, ortho and para toluidine and when the time for naphthol dyes came, the demand for pure xylene and xylindine also appeared. The higher homologues which could only be isolated and nitrated with difficulty were still left in the solvent naphtha as before, the more as through Hofmann's "method of wandering of atoms in the molecule" (mobcular re-arrangement)—a synthetic process for the preparation of cumidine and other aniline homologues was given.

In this progressive movement from the originally incomplete-ly separated and purified tar distillates to the uniformly thiophene-free materials, out of which the industry is forming its synthetic structures to-day, we find for the first time the characteristic reciprocal action between theory and pracice to which the coal-tar colour industry owes its unprecedented rapid development. According to the precedence of Hofmann and Nicholson the leaders of science and industry go hand in hand, one with another in times to come. The factories gladly put their observations and experiences gained in connection with products and by-products obtained on large scale at the disposal of scientific investigation. Therefrom new materials and new working methods emerged for the industry as practically realizable informa-tions on the nature of their products and processes. And when

Alizarine industry. (*Even to-day approximately correct data of the annual production of anthracene is found. in Schultz', Chemie des Steinkohlenteers II, 597. In* 1890 6000 *tons of crude anthracene equivalent to* 1800 *tons of pure anthracene worth* 4.75 *million marks were imported to Germany. The German production amounted to about* 400 *tons of crude anthracene. In return Germany exported anthracene dystuffs worth* 12½ *million marks*). Neither in Switzerland nor in France or Austria Alizarine industry was able to hold its ground and in England after hard struggle for competition it has again lost the ground within the last decade. It was a result of the prominence once attained by the German technique.

Purification of Anthracene :

The purification process of anthracene was further explained to us. It consisted in its working up to anthraquinone or dichloroanthracene, in a more or less complete extraction of the easily soluble attendants of crude anthracene by dissolving in petroleum naphtha and in a final sublimation, or by a previous treatment with molten caustic potash for the removal of carbazole in the form of its potash salt. Early the industry had discovered this process and had established it by the analysis of anthraquinone. Also in the separation of the accompanying substances of anthracene, industry had been ahead of science. Soon, however, and often through joint investigations by their representatives [*Graebe and Gläser, (Carbazol*) *Ann. d. Chem.* 163, 344; *Graebe and Caro (acridine) Ann. d. Chem.* 158, 265] theory and practice began to attack the more easily accessible region of the high boiling tar distillates, so that within the last two decades, especially by the works of Graebe and Liebermann as well as of Baeyer, Perkin and Fittig, Behr and Van Dorp, Bernthsen and Bamberger and other investigators—a comprehensive knowledge had been attained not only of the anthracene and its derivatives but also of the acridine and carbazole groups, of the methyl anthracene and phenanthrene, of acenaphthene. flourene, pyrene and chrysene, partly also an insight into their synthetic mode of formation from benzene or napthalene derivatives and—far ahead to the earlier experiments by Berthelot—in the pyrogenic

formation of tar distillates. However, the practical realization of this knowledge was uptil now principally confined to the anthraquinone dyestuff industry. From carbazole only recently a useful yellow dyestuff had been prepared; acridine has won some importance only as an indirect mother substance of a group of synthetic dyestuffs; phenanthraquinone and diphenic acid had failed like anthrol, anthramin or diamnofluorene to fulfil the expectations and from the series of other solid hydrocarbons mentioned, no derivative had as yet come to experimental application. Therefore an extensive field for the future development of coal-tar. dyestuff industry lies still unexplored.

Naphthalene Desivatives :

We now enter the store-house of pure naphthalene and we hear that this raw material, present in tar, ten times more than the quantity of anthracene. from which it is so easily separated in pure condition, has attained industrial significance for the last 16 years only. Formerly it had found only little application for the preparation of dinitronaphthol and Magdala Red. A correspondingly small quantity of α-naphthylamine was produced for that purpose and for the former also α-naphthol. Chloro-oxynaphthalic acid and phthalic acid have only reached the experimental stage. Roussin's artificial Alizarine has proved an un-utilizable Naphthazarine in the beginning. For a long time naphthalene was charged with the prejudice of worthlessness as all attempts to apply the aniline dye processes on naphthylamine had led to ugly and non-fast colours. Only since the discovery of Phthaleins. and the introduction of β-naphthol in the industry of azodyes, this prejudice has been removed. And with the increasing investigation into the domain of naphthalene, of the technical synthesis of β-naphthylamine and its secondary bases, of the production of numerous sulpho-acids of isomeric naphthols, naphthylamine, aminonaphthol and dioxynaphthalene, into the discovery of phosgene colours of the benzene and naphthalene series as well as of the Rosinduline and the Napthol Yellow S, of the final utilization of Naphthazarine by the application of modern chrome mordants etc., and increasing number of naphthalene dyes have entered the industry emulating in beauty

with those of the aniline dyes or in fastness with those of the anthraquinone group. At the same time they were cheap and simple to manufacture. So naphthalene was more and more recognized as a principal source of just those coal-tar dyes which were called for to replace the still existing cheap wood dyes and some of the formerly used aniline dyes. The explosive industry also had come to utilize the nitrated naphthalenes.

Position of Phenol :

"However in this branch of modern explosive industry"— the guide tells us—as now we cast a glance on the stores of pure carbolic acid—"phenol in the form of picric acid finds a predominating application. Some years ago the sudden demand could scarcely be met and one began to prepare it temporarily from benzene. For, as it is well known, the antiseptic as well as the industry of salicylic acid and its preparations consume enormous quantities of carbolic acid. The increasing demand has resulted, however, especially in Germany in a rapidly increased recovery of phenol from the crude carbolic acid and even if one estimates its average content in the tar as only about 1.5%, there is no danger of further scarcity. At the same time the industrial recovery of cresol was developed. In dyestuff industry phenol serves as a starting material for a series of valuable azodyes, derivatives of anisole and phenetole, of dianisidine and ethoxybenzidine as well as chiefly of the salicylic acid. As substitute for the latter the homologous ortho-cresotinic acid also has been used recently. · But the extensive use of coloured phenol derivatives, picric acid and coralline, Kolbe and Schmitt's Rosolic Acid has been greatly reduced now by much better red and yellow dyestuffs."

Runge's Discoveries :

"Was not"—we ask—"the Rosolic acid the oldest artificial dyestuff? Is not the merit of its discovery and therewith also the establishment of the coal-tar colour industry due to our gifted countryman Runge? Has not this investigator by his first pioneering investigations on the coal-tar distillates discovered aniline, carbolic acid and quinoline, together with the magnificent

colour lake of Rosolic Acid already in 1834;" (*Runge, Poggendorff's Ann.* 31, 70).

"From the ·scientific standpoint"—is the answer—"tl.* discovery of these substances in coal-tar is indeed imperishably connected with the name of Runge. However, the dyestuff industry does not lead back its establishment to this discovery. Industry counts the utilization of the scientific discovery for the manufacturing life only. Runge had discovered Rosolic Acid and he had been even aware of its colouring nature, but there was still the third decisive moment missing : the industrial application. The discoverer thought of it but did not apply it. This was as impossible as the utilization of colour reactions of aniline which he observed in numerous cases and therefore named it blue oil or 'Kyanol'. Neither the most sparing quantity of Kyanol which was recovered from the base mixtures of a tar, nor the Rosolic Acid derived from a little known by-process, could form the foundation of an industry. Runge's discovery came ahead of its time—the coal-tar benzene and the technical method for the preparation of aniline was still lacking. However, his first but only qualitative investigation of the tar-colour distillates was the seed corn for the future harvest and when the warm sunshine of scientific knowledge fell on this it attained its germinating power principally under Hofmann's care. It was Hofmann (*Hofmann, Ann. d. Chemie,* 47, 37) who in the spirit of Liebig's methods of investigation by the elementary analysis and with the potash apparatus proved in 1843 the identity of *kyanol* with the *crystallin* produced previously from Indigo, as well as its identity with Aniline of Fritzsche and with the *benzidam* of Zinin. Hofmann first recognized the genetic relationship between 'phenamid' and 'phenylhydrat', or the carbolic acid, which had previously been closely studied by Laurent, and henceforth Hofmann selected the domain of aniline as his favourite field of investigation. Then followed the next step. The branch grew and when in 1856 it was amalgamated with the ancient trunk of the chemical industry by Perkin, the pupil of Hofmann, there emerged from it the branch of our coal-tar colour industry with flowers of magnificent hues. Then very soon synthetically pre- pared Rosolic Acid followed Rosaniline and the first light fell on the constitution of our coal-tar colour groups from the later

knowledge of the genetic relationship between the aniline and phenol-dyestuffs.

Our guide concludes,—"if one wants to trace back the origin of the industry—the oldest of its coloured products, one has to mention Picric Acid, known since 100 years and which produced from Runge's carbolic acid found its way into the dye industry shortly before the discovery of the first aniline dye. It remained however an isolated sprout and had no lasting influence on the development of this branch of industry. In the explosive industry only its characteristics attained presumably the lasting importance; as a dyestuff its application has been replaced more and more by better materials. The branch has shown its own direction to the sprout."

Intermediate Products :

An extensive group of factory buildings lie before us. "These are the workshops for the intermediate products"—goes the explanation. "Here the most important working methods are adopted, to which the domain of aromatic compounds owes their extension. Their handling is dictated by the theory for the preparation of the raw materials and with great energy it is carried out into actual practice. Some of the products thus obtained can be directly used in industry and form independent commercial commodities, the majority however are utilized as building elements for the synthetic composition of our dyestuffs, medical and luxury goods. Sometimes science, sometimes practice have evolved in continuous mutual action with one another the methods of approach or have adjusted them to new objectives or developed the technique of their own practice. Very little of it was present at the beginning of the industry, and this little often met with mutual prejudice and the former mistrust existed between empiricism and science. However, all this has changed along with our progressive development. Now-a-days if one needs a new tar derivative of definite power of action, here or there a smooth path is found jointly and every newly discovered method opens up simultaneously to a new scientific and technical field of work. So, in a certain sense, our chemical methods have become comparable to the procedure of the mechanical technique
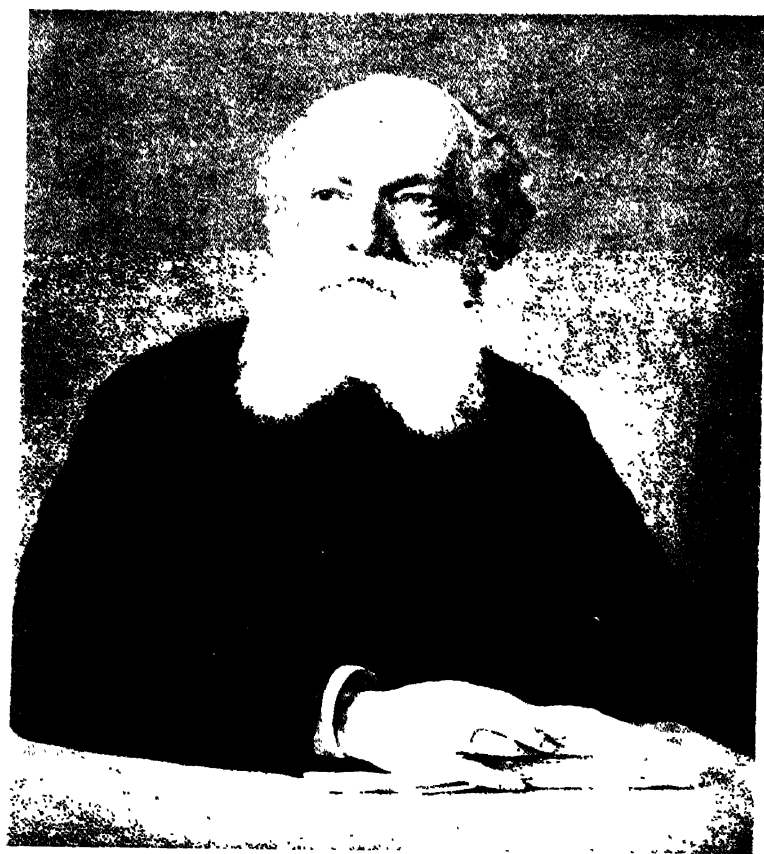
AUGUST KEKULÉ (1829–1896)

FRIEDRICH AUGUST KEKULÉ

1829 – 1896

Kekulé was born in Darmstadt, Germany on the 7th September, 1829. His father Carl Kekulé was a Head clerk in the war office. Young Kekulé was meant for the study of architecture at the University of Giessen but fascinated by the skill and genius of Liebig, whose lectures he attended in spare hours, decided to "abandon the architecture of houses for the sublimer architecture of molecules." He studied chemistry at Giessen with an uncommon zeal and industry of which he has given the following description when he became a famous man : "If you want to be a chemist", said Liebig to me when I was working in his laboratory, "You must ruin your health with study ; he who does not ruin his health with study can add nothing to chemistry now-a-days." I faithfully followed his advice. During many years four and even three hours' sleep was sufficient for me. One night spent waking over the books was not counted at all, it was only when two or three came in succession I thought that I have done something meritorious." In July, 1852 Kekulé obtained the degree of Dr. Phil. at the University of Giessen. From May, 1851 to April, 1852 he studied in Paris with Dumas, Wurtz, Cahours, Gerhardt, Regnault and Pouillet. For some time he worked as an assistant to a chemist in London. In 1856 he became a private-docent at the University of Heidelberg. There in 1858 he published his memorable paper "On The Constitution and Metamorphoses of Chemical Compounds and on the Chemical Nature of Carbon." The immediate result of this famous publication was that he was called to the Chair of Chemistry in the University of Ghent. Here he published his classical *Lehrbuch der Organischen Chemie* and in 1865 he developed the famous Benzene Theory. The publication of the benzene theory is regarded as one of the greatest events in the History of Chemistry, and its 25th anniversary was celebrated in Berlin by the German Chemical Society in 1890. This was attended by chemists from all over the world. It needs no mention, however, that but for the benzene theory it would not have been possible to gain an insight into the constitution and relationship of the complex hydrocarbons (like naphthalene, anthracene, phenanthrene, etc.), as well as the heterocyclic compounds (pyridine, quinoline, thiophene, etc.) and their derivatives. The Benzene Theory has not only enriched the scientific chemistry but it has also exercised a profound influence on industry. The dyestuffs are the children of benzene and their systematic synthesis including the elucidation of constitution and ultimate syntheses of Alizarine and Indigo would hardly have been possible without this epoch-making discovery of Kekulé. The same is true for host of other organic compounds. Nothing could better express the fitting recognition of Kekulé's contribution to chemistry than the following utterance of Hofmann—*" Alle meine Entdeckungen gäbe ich hin gegen den einen Gedanken Kekulé's "*. In June, 1867, Kekulé was called to Bonn as

successor of A. W. Hofmann to take charge of the newly erected laboratory designed by Hofmann. There he continued to teach and inspire students with his supe b personality until his death in 1896. Among his famous pupils the name of Baeyer, Körner, Ladenburg, Dewar, Anschütz, Thorpe and Van't Hoff deserve special mention Kekulé will ever be remembered as a brilliant chemist, a great teacher and a lovable man.

only that there it means the change of form of a lifeless mass, whereas here it is the material metamorphoses of the molecules endowed with energy, and we are not capable as yet to calculate beforehand the full 'technical effect' of our figures with the precision of the engineer. We must still verify it through experiments first. The rules of our construction are still defective. However, as one welds, rivets, solders, couples, joins, constructs according to the design till from the clumsy or un-yielding piece of work the machine part or the part of the build-ing material is formed, so also do we send our raw materials from one hand to another—chlorinate, brominate, oxidize, reduce, condense, add nitro, amino, sulpho-groups, carboxyl and hydroxyl, devise chains and rings till every atom in the forma-tion of the structure of the new molecule has taken up the place which has been sanctioned and assigned by the theory. From the point of view of working methods we, therefore, like to cast a glance into the smithy and workshop of our intermediate products."

And we ask,—"Which theory rules the systematic applica-tion of these methods?

"Kekule's Benzene Theory, the theory of aromatic com-pounds. It has created order amongst the present stock and into the future it has thrown its light. Its clear, uniform significance of the widely scattered facts, its explanation, of the formerly enigmatical isomerism, the search for its predicted results, whose connection with one another to distinct groups and series, ortho, meta, para-, the stream of chemical investigations which over-flowed the newly opened domain of space and structural chemistry with its increasing number of younger investigators—the laboratories were too narrow, they had to be extended, the amount of new problems and methods put forth to test the theory—this new doctrine—which declared in the original field of coal-tar colour technique, benzene as the mother substance of the aromatic compounds. And soon after the establishment of the theory there was no longer necessity for prediction in the hieroglyph of types to the scholar but now only in the generally comprehensive language of the structural formulae. All this did illumine like a brightly dawned day the former dark path of

industry, and its progress on the sure path to far-off recognisable aims did powerfully accelerate. With the advent of Kekule's brilliant theory a new era had dawned for the industry also. The latter felt that it had to keep pace with the progress of science to which it owed its origin and whose leaders had become also its leaders. The handling of the more refined methods was no longer to be entrusted to uneducated workers and supervisors —the locksmith's handiwork had become the fine mechanics! *One sought for scientifically trained manager for the works,* scientific laboratories were erected in the factories and the results were soon obvious. Where first theory emerged into flesh and blood of practice, where it found its numerous research workers, inspired masters taught, there it bore also its first industrial fruits. That happened here. It caused our first and most powerful lead."

Nitration Section :

On our entrance to the next factory area the bitter almond-like smell of nitrobenzene greets us. At first glance we perceive that nitrations are performed here. Long lines of apparatus arranged in the form of a terrace : cast iron cylinders with mechanical stirring and external cooling arrangements, over them stone-ware pots with nitrating acids confront us. "Here," says the guide—" we insert once or more often, the nitrogroups in the benzene nucleus of our tar distillate into the positions indicated by the theory, or we nitrate those which have arrived here previously sulphonated, aminated, chlorinated, etherified or otherwise previously formed derivatives coming from other factories. Here we separate also, as far as necessary and practicable, the mostly simultaneously formed isomers according to the rules which the scientific finishing of Kekule's theory has taught us, and is teaching us daily anew. The nitration is one of our oldest and most widely used methods. It still serves its main objective discovered by Zinin; namely, the indirect introduction of amino group into the benzene nucleus of the aromatic compounds, as also the preparation of azo-compounds introduced by Mitscherlich; production of analogues of Zinin's azoxybenzene, as well as the formation

of hydrazo-compounds, explained by Hofmann, and their re-arrangements to the recently so successfully utilized diphenyl bases. For this reason the products obtained here, are mostly sent to the reducion works; however, many are previously sulphonated or etherified and so forth, or find their direct application in the dye-departments, as for example the paranitroaniline and metanitrobenzaldehyde, the nitrobenzene in the Fuchsine processes or the dinitronaphthalene in the manufacture of Naphthazarine.

For the method of nitration and its numerous applications we are thankful to theoretical investigations. In fact we still nitrate in the same way as Mitscherlich produced nitrobenzene in 1834, the year rich in discoveries, likewise Laurent introduced nitronaphthalene one year later, and as later on Deville produced dinitrobenzene and Arppe the paranitroaniline. Even now we apply the nitrating mixture of nitric and sulphuric acids as Hofmann and Muspratt did in the preparation of dinitrobenzene for the metanitroaniline discovered by them in 1845. On the other hand the industry got the task to ascertain the industrial significance of the numerous existing nitro compounds and their analogues and to make possible the often very difficult process of execution on a large scale. In many cases this task has been successfully solved while in others it has failed. Although one had succeeded by the careful study of the reaction-conditions, to fashion the nitration of easily oxidizable substances to a smooth running operation, as for example, to prepare nitro-cinnamic acid or nitrobenzylchloride on a commercial scale, in the end the economy of the process failed completely by the simultaneous formation of the ortho and para isomers. Otherwise the commercial problem ot artificial Indigo would have been solved years ago. The ortho compounds only are required for the purpose. However, a manufacture cannot be dependent on the utilization of its side products. The conditions of the formation of the isomers requires further scientific explanation.

During our visit to the extensive nitration workshops the technical details of the process of manufacture of the various nitro compounds are explained to us. We observe how one operates according to the energy of reaction in long or short

time, at ordinary or higher temperature, or much below the freezing point. When surprised to see blocks of ice—the guide tells us—that the "ice cooling" everywhere practised in scientific laboratories has come to be commonly used in the coal-tar colour industry only in the last decade. Formerly some of the old experts might have thought this to be "too scientific". "Let nature follow her course" they said. In summer many things could not be produced. The diazotizer had first of all insisted on the use of ice. With the progressive development of the azodyestuff industry the ammonia-ice machines of Linde were introduced in the factories, and now artificial ice is applied wherever it is serviceable. This resulted in an expansion of their ranges of operation and the increased economy and safety of their processes have powerfully influenced the progress of the industry.

About nitrobenzene, it is remarked, that fortunately it has become the forerunner of the modern artificial perfumery even before the discovery of aniline dyes. In France it was first brought to the market as a substitute for the then costly oil of bitter almond by Laroque and Collas and it soon found its way to the technical production of aniline. However, the existing manufacturing methods of nitrobenzene for extended purposes had to be altered immediately. In place of earthen ware pots and spiral pipes, iron apparatus were introduced which had first been constructed at Nicholson's factory, and which are still in use. The secret of this nitrobenzene and aniline cylinder belonging to it have been carefully guarded until simultaneously with the process of formation it has spread every where by its constructor. This has accelerated the development of the aniline industry to an extra-ordinary degree. From these apparatus the industry learnt the use of cast iron in nitration and the reaction-promoting power of mechanical stirring.

Finally the interdependence of the chemical methods is explained to us with the help of a nitration, just going on.

"It is a difficult piece of work"—says the guide. "First three sulphogroups have been added to naphthalene by the sulphonators. Here a nitro group is introduced to it. It will then be replaced in succession through reduction. diazotization

and boiling by amino, diazo and hydroxyl groups and finally the naphthosulphondisulphonic acid formed by the caustic fusion converted into the corresponding peridioxynaphthalene disulphonic acid with fixed position of its groups at 1 : 3 : 6 : 8. Then the whole will serve for the structure of still more complicated azodyestuffs from the new and interesting groups of chromotrope" (*H. Koch* 1890, *D. R. -P.* 56058).

We remarked that we did not surely expect such scientific explanation from the mouth of a factory chemist. "The chemists in the factory have to master such things now" said the guide.

Amination or Reduction Section :

In the adjacent aniline works with the huge reduction cylinders and distillation stills in the manufacture of toluidine and xylidine, of ∝-naphthylamine and the metadiamines we found Bechamp's amination method (*Bechamp*, 1854, *Ann. Chim. Phys.* 42, 186) exercising its undisputed monopoly. This method, originating from science, has, as we heard, essentially contributed to the establishment and rapid development of the aniline industry. It was a lucky coincidence that Perkin, before his discovery of the first aniline dye became fully conversant with this method in Hofmann's laboratory. There, its advantage over the then known reduction methods was tested. Hofmann recognized its high value and recommended it warmly in word and writing for the reduction of all types of nitro-compounds (*Hofmann, Proc. Roy, Soc.* 1885, 1, 444). Chiefly for the preparation of aniline the method was adopted in his laboratory and with the naphthylamine obtained by the same method, Perkin undertook his first published investigation there. So already at a very early date the direction was given to the technical production of aniline and its analogues; without delay the reduction of nitrobenzene by Bechamp's method was adopted. To the uninitiated this way however, remained hidden for several years to come. Long after the commencement of the industry many attempted still to obtain aniline from heavy oil or from nitrobenzene according to the prescription of old text books, particularly by Zinin's method. For laboratory purposes one stuck for a long

time to the process of potash fusion of Indigo. Zinin's pioneer-
ing amination method however was qualified only for the fulfil-
ment of its scientific mission; with the clumsy, costly and often
incomplete reduction with ammonium sulphide the present annual
production of several thousands of tons of aniline and its
analogues would never have been possible (*the annual production
of aniline, toluidine etc., amounts to about* 8000 *tons of which*
$\frac{1}{5}$ *in England*). For that purpose Bechamp's method proved
most suitable. One had to develop only the mechanical handling
to replace the iron filings by cast iron borings and later also to
replace acetic acid by the cheap hydrochloric acid. Thankfully
the industry accepted this gift of science and wherever possible
promoted its progress through the products and by-products of
the new commercial methods. One such by-product led, for
example, to the discovery of the aromatic diamines.

About this discovery we learn the following:

In the course of his investigations on the ethylene bases
Hofmann did not succeed in obtaining the aromatic analogues
of ethylenediamine. The description of the semibenzidine
produced from dinitrobenzene by Zinin did not encourage him to
experiments in the same direction. Hofmann and Muspratt in
their similar earlier experiments could also advance up to
nitraniline only. It was therefore a welcome gift which the
industry gave to science in the metatoluylenediamine. From a
French aniline factory a well crystallized by-product was sent to
Hofmann (*Hofmann, Proc. Roy. Soc.* 11 (1861) 518). It
proved to be the said base and its origin was explained by the
impure nitrobenzene containing dinitrotoluene which was used
in those days. A direct reduction experiment with pure
dinitrotoluene according to Bechamp's method confirmed this
explanation. In the same way dinitrobenzene and metanitroani-
line produced the long looked for phenylenediamine. This
discovery of the aromatic metadiamines led quite naturally to the
reduction of Arppe's p-nitroaniline and thereby to the dis-
covery of p-phenylenediamine and its close relationship to
the quinone (*Hofmann, Proc. Roy. Soc.* 12, (1863), 639).

This gift of the industry bore still further fruit. It caused
a thorough investigation of the *queues d'aniline,* the high boiling

distillation residues ' of aniline. Besides metatoluylenediamine Hofmann separated therefrom a large quantity of p-toluidine also (*Hofmann, Proc. Roy. Soc.* 12, (1862), 312, 389) and used it for a renewed investigation (*Sell, Ann. d.. Chemie* 126, 153) further for 2 new bases: the still unexplained para-aniline and xenylamine, our present p-aminodiphenyl. On the other hand, paraphenylenediamine led to the discovery of the general methods of formations of paradiamines by the reducing fission of the corresponding aminoazo compounds. The diphenin, obtained by Gerhardt and Laurent as an intermediate product from dinitroazobenzene, split up in Hofmann's hand into two molecules of paraphenylenediamine by energetic reduction (*Hofmann, Proc. Roy. Soc.* 12, 644). Finally, the discovery of the isomeric diamines stimulated the idea regarding "two similarly related monoamines of the phenyl series" originating in aniline derived from different sources and hereby Hofmann found his previously mentioned pioneering explanation of the industrial mode of formation of Rosaniline.

"The German aniline industry"—concludes the guide—"has also rendered a similar service to science almost at the same time. The discovery of the fundamental cases of isomerism in benzoic acid series may be traced to the investigation of a by-product in the nitrobenzene manufacture (*Fischer, Ann. d. Chem.* (1863), 127, 138), which a former student of Kolbe placed in huge quantity at the disposal of his professor. This by-product which shortly before Beilstein claimed as Nitrodracylacid, an isomer of nitrobenzoic acid (*Ann. d. Chem.* 126, 255; 128, 257; 132 137) served finally Beilstein for the establishment of completely explained isomerism of paranitrobenzoic acid and its amino and oxyderivatives (*Ann. d. Chem.* 132, 309) together with those previously known direct derivatives of benzoic acid now shown to be identical with salyl and dracylacids. The material used by Beilstein came also from a German nitrobenzene factory. (*Ann. d. Chem.* 132, 144 comment). So from early times, the aniline industry has contributed much towards the recognition and explanation of significant cases of isomerism."

A further example of this fruitful reciprocal action between theory and practice becomes evident from the preparation of orthotoluidine.

Also for the discovery of this base—we hear—one has to be thankful for the impetus given by Hofmann to his explanation of the formation of Aniline Red.   In a surprising contradiction to this explanation Coupier (*Coupier, Bull. Soc. Ind. Mulhause* 1866) soon afterwards prepared a liquid toluidine from benzene-free toluene, which in spite of the complete absence of aniline still proved to be eminently capable of producing Toluene Red, a colouring substance similar to Aniline Red.   By a careful test of this mysterious toluidine Resenstiehl (*Rosenstiehl, Dingl. Polyt. Journal* 181, 1866, 389, *Zeitschr. Chem.* 1869, 189) then found in it besides paratoluidine a new isomeric base, called pseudotoluidine as an active constituent, and ascertained an exact method of separation which led back to the origin of both the toluidines by simultaneous formation of a solid and liquid nitrotoluene during the nitration of the substance which was previously considered as a uniform or unmixed toluene.   Thereby he recognised that according to the conditions of nitration these isomers are formed in variable proportions.   Earlier Jaworsky and then Kekule' (*Kekule', Zeitschr. Chem.* 1867, 225) separated the solid *p*-nitrotoluene but only by Beilstein's and Kuhlberg's comprehensive investigations (*Ann. d. Chem.* 155, 1; 156, 66) in 1870 the nature of the liquid parts as well as the entire field of isomeric nitrotoluene and toluidines have been explained in a directly profitable manner.   Now dyestuff technique proceeded from the already establishd separation of its homologous raw materials to those of their isomeric intermediate products.   In the factories improved methods of separation were searched for and this with such good results that now-a-days they have at their disposal any quantity of ortho and paranitrotoluenes as well as ortho and paratoluidines.   The industrial value of the orthotoluidine has made itself known first of all in the manufacture of Safranine (*Cf. Hofmann and Geyger, Ber.* 1872, 5, 532) and that of orthonitrotoluene in the manufacture of Fuchsine.   Paratoluidine found a rich field of employment only in the young industry of its sulphur containing derivatives, the Dehydrothiotoluidine and Primuline and since the discovery of the substantive azodyes ortho and paranitrotoluene became starting materials for valuable orthofoluidine and paradiaminostilbene dyestuff.

As a natural consequence the processes of formation of Aniline Red and Toluene Red now offered an occasion to seek for analogous Xylidine Red and at the same time to the investigations and separation of crude xylidine (*Hofmann, Ber.* 2, 377). On his return to Germany also these works have been undertaken by Hofmann in collaboration with the friendly aniline manufacturers, in part even in their factories. (*Hofmann, Ber.* 2, 411; 4, 1292). Later investigations by the younger investigators have perfected the knowledge of isomeric xylidines (*Noelting und Forel, Ber.* 18, 2669) but only in the industry of azodyes uniform products were obtained, particularly the metaxylidine, easily separable in the form of its acetate, and rose to industrial importance.

During our further wandering through the reduction departments we met here and there with the application of tin and zinc dust instead of various modifications of Bechamp's method. We were told that the technical preparation of naphthylamine by Roussin in 1861 and later on the application of tin and hydrochloric acid for the reduction of nitro compounds recommended by Beilstein remained to a great extent confined to scientific purposes (*Beilstein, Ann. d. Chem.* 1864, 130, 242). Nevertheless this elegant and safe laboratory method enabled the first preparation of Hofmann's metadiamine for the production of Phenylene Brown, the oldest commercial azodyestuff (*H. Caro, Manchester,* 1864). Of course on a large scale, tin was displaced not by H_2S but by zinc and taken back to the process. However, the industry learnt a few years afterwards to make use here also of the cheaper iron. Only in isolated cases the smooth and energetic reducing action of tin and hydrochloric acid was still not dispensable. On the other hand zinc dust was used more and more in the dyestuff industry since its first industrial application for splitting up aminoazotoluene into toluidine and para toluylenediamine for the manufacture of Safranine (*Witt, Ber.* 12, 939). With its help one also obtained from aminoazo and nitroso compounds in the factories of Methylene Blue, of Safranine and other dyestuffs—the paradiamine which was used there directly. In the province of intermediate products zinc dust chiefly serves for the preparation of azobenzene as well as for the intermediate formation of Hofmann's

hydrazobenzene and its analogues for their rearrangements into Zinin's benzidine and the related diphenyl bases as explained by Hofmann (*Hofmann,* 1863, *Proc. Roy. Soc.* 12, 576).

This method of reduction is illustrated to us in its extensive applications. Its condition consists of the gradual addition of the required quantity of zinc dust into a constantly stirred mixture of nitro compounds in aqueous sodium hydroxide solution. This method also came from the industry (*August Clemm* 1868. (*Bad. Anilin und Sodafabrik*). Soon afterwards *Alexeyeff published the use of alkaline zinc dust reduction in alcoholic solution.* (*Zeitschr. Chem.* 1868, 497). Amongst its contributions one found Induline (*N. Handwtb. Chem.* 3, 794) as well as the first industrial utilization of benzidine for the production of its tetranitrodiphenyl derivative and the fast dye 'Palatin Orange.' But only 15 years later with the discovery of Congored and Chrysamine, the time for its great and lasting technical importance began for the manufacture of benzidine and its analogues. Scientific investigations in the meantime had prepared the field of diphenyl bases for the later harvests. (*G. Schultz, Ann. d. Chem.* 207, 311). The material now being easily available, there was lively interest in the preparation of new non-mordanted cotton dyes. The competition of the manufacturers to obtain patents, released a rich store of new investigations on the formation and capacity for rearrangement of the hydrazo-compounds, on the preparation and properties of new diphenyl bases or similarly applicable compounds. Investigations clarified (*Ber.* 21, 3138; 23, 3252; 18, 3254; *Chem. Ztg.* 1885, *No.* 25) not only the so long unexplained specific activity of the paradiamine but also the influence of the position of substituted groups on the same. It further opened new methods for the preparation of stilbene derivatives and oxydiphenyl bases of azoxy-compounds and methyl benzidine (*Bender & Schultz Ber.* 19, 3234; *Weinberg, Ber.* 20, 3171; *Sandmeyer D. R. P.* 1888 *No.* 52839). These results were worked out in the laboratories of the academic institutions and dyestuff factories. They were equally useful to science but have furnished the industry only with ortho-dianisidine, diaminostilbene disulphonic acid and ethoxy benzidine as frequently used intermediate products besides benzidine and orthotoluidine. Also from diamino-

carbazole and paraphenylimdianine useful dyestuffs of this group were produced. After the latter had become ascessible, it found an extensive field of action in the manufacture of aminated water-soluble Indulines. Before we left the reduction department we were shown, in addition to the manufacture of   ⍺-naphthylamine and some of its isomeric mono and disulphonic acids, the application of an amination method whose discovery was due to the empiricism. (*H. Caro, Holdmann, D. R. P.* 1880, *No.* 14612; *Bad. Anilin und Sodafabrik* 1879). This is the conversion of   β-naphthol and its sulphonic acid into the Liebermann's β-naphthylamine and its corresponding derivatives.

What once Laurent and Hofmann tried in vain in the benzene series to revert phenol into the amine (aniline) by heating with ammonia has been realized by the industry in the preparation of its naphthalene dyes.   β-Naphthylamine, formerly a costly laboratory preparation, is now since a decade, in combination with a series of new and manifold verified derivatives, a commercial intermediate product in the azodye industry; at the same time it has promoted the scientific understanding of the isomeric relation in the domain of naphthalene, principally by the latest works of Armstrong and Wynne. (*Proc. Lond. Chem. Soc.* 1890, 1891). We heard further how industry with its new methods of working has understood to produce the valuable   β-naphthylamine derivatives straight from the inferior quality sulphonation products of   β-naphthol (*Brönner, D. R. P.* 22457; *Landshoff, D. R. P.* 27378; *Cassella, D. R. P.* 43740, 46711) and ultimately penetrated into the nature of its new materials (*Baeyer and Duisberg, Ber.* 20, 1426, *Weinberg, Ber.* 20, 2906; *Pfitzinger and Duisberg, Ber.* 22, 396). It was a further sign for its progressive rational thinking and method of working. The method itself, however, they tell us— owes its origin to one of those hazardous analogous conclusions which mostly lead the empiricist to his surprising discoveries. The scientific explanation then opens the path to systematic investigations. The success of Hofmann's cumidine synthesis in the manufacturing of *Höchster Ponceau* has inspired experiments to the hydrochlorides of the primary amines with reactive naphthylalcohols instead of the aliphatic alcohols. The significance of a new product thus obtained as   β-naphthylamine

has stimulated at once the study of the influence of ammonia on naphthols. (*Graebe, Ber.* 13, 1850).

Now science also has taken notice of the new process (*Merz and Weith, Ber.* 13, 1298; 14, 2343; *Calm, Ber.* 15, 609; *Benz, Ber.* 16, 8; *Merz and Müller, Ber.* 19, 2901), and by more scrupulously investigating the reaction-conditions with the help of zinc chloride-ammonia has finally succeeded in preparing in quantity aniline and diphenylamine from carbolic acid. Although the old problem had been solved, the solution came nevertheless too late to be of use to the highly developed technique for the production of a mixture of bases. For aniline, Bechamp's method still remained valid. For the diphenylamine, however, the phenylation of aniline had been found long ago by the dyestuff industry.

This process of phenylation we met with in the next compartment where the aminated products are further worked up to their secondary and tertiary derivatives by alkylation, benzylation, phenylation etc.

On the introduction of these methods into industry we heard the following: During empirical experiments with the then New Fuchsine Girard and de Laire observed towards the end of 1860 that the red dyestuff by heating with aniline gradually changed into a magnificent violet and finally into a spirit-soluble blue of great colouring power. At once the industry got hold of this valuable new discovery. Hofmann (*Proc. Roy. Soc.* 13, 9) began scientific investigation of this mysterious process and announced in June 1863 that Aniline Blue is a triphenylrosaniline —a surprising interpretation of his analytical results.

Thus industry had quite unconsciously utilized on a large scale the long missing method of phenylation. Up to then one had tried in vain to replace halogen alkyls which had been used with unique success by Hofmann through their analogues of the phenyl series. Phenyl chloride, bromide and iodide behaved indifferently in all substitution experiments, not explainable then. Now it became known that the amine is the active agent.

The wonderful change of colour from red to blue by the presence of phenyl in place of hydrogen stimulated the question: What will be the reaction of an analogous substitution by the

more accommodating alcohol radicals? Readily the experiment with iodides is done, and Hofmann describes the result in the following words:

"I cannot describe the pleasure with which I noticed the intensive blue colour of the mixture of Rosaniline with these iodides, as I took out the pressure tubes from the bath after one day's digestion."

Thus Hofmann's Violets were discovered! A series of dyestuffs of unexpected beauty with shades from the deepest red to the most blue violet.

Of great importance was this discovery for the development of the coal-tar colour industry. Not only through the addition of new products but much more by the ennobling inluence which the inoculation of purely scientific methods of investigation began to exercise on the stem of the chemical industry. Although the first news of the industrial production and utilization of aniline— a laboratory preparation had indeed astonished beyond measure the manufacturer and the undeniable commercial success of Mauve and Magenta compelled him for the first time to take in hand a modern text book on organic chemistry and with hard toil to acquire a scanty knowledge of Hofmann's and other investigators' works to work his way toilsomely through the peculiarly sounding, often unpronounceable long names and fearfully typical manner of writing and to obtain at least a little aniline by the distillation of Indigo or to procure it at great expenses from a merchant and began to experiment and investigate in the light of work done in the field of dyestuff chemistry— the methods being still quite simple and easily comprehensible. Either one oxidized in aqueous solution as in the case of Aniline Violet or by a fusion processes as in Fuchsine. The reagents were of inorganic nature and available in the factories. Finally one boiled the dye with aniline according to the method of Aniline Blue. But now Hofmann's Violet! methyl iodide, ethyl iodide, amyl iodide! Bromides of methyl, ethyl, propyl, amyl and capryl! Primary, secondary and tertiary amines,' probably also ammonium base! Who had at any time heard or seen something in a chemical factory, which manufacturer could deal with similar scientific things could set his energy and his capital on patent processes like this? (*Hofmann, E. P.* 1863, *No.* 1291).

This only a professor could believe. The costly iodine, bromine and the inflammable phosphorus!. Where were the pressure tubes?

At that time still many a practical man of the old school was thinking in this way. But Hofmann's student Nicholson did not think so; he manufactured the Iodine Violet. It had epoch making success and the prejudice against the application of scientific working methods in factories of industrial worker was removed for ever. Now every body had to be in it. One tried to acquire all the helping agents which up to that time had furthered the development of organic chemistry. The word 'alcoholic radical' reminded of Frankland's digestor, and the autoclave came into existence. The dye maker boiled his Iodine Violet in the champagne bottle tightly wired.

Very soon a new impetus followed. In order to gain an insight into the constitution of substituted rosanilines Hofmann investigated [Hofmann, (1864), Proc. Roy, Soc. 13, 341; Ann. d. Chem. 132, 160] the products of their dry distillation. While Rosaniline produced a large quantity of aniline, he obtained ethylaniline from the Ethyl Violet already existing in commerce. Now the long fruitlessly sought for phenylated aniline—the diphenylamine also was found by the same treatment of phenylated rosaniline. This expectation was confirmed by an experiment undertaken on a large scale of by Girard. From the distillation products of Aniline Blue sent to him Hofmann isolated the diphenylamine and in an exactly similar way obtained shortly afterwards the expected tolylphenylamine from Toluidine Blue prepared by heating Rosaniline and p-toluidine. (Hofmann, Proc. Roy. Soc. 13, 485; Ann. d. Chem. 132, 289).

These new secondary bases now showed outstanding colour reactions, which led to their technical preparatoin. Theory has indicated the path and one had only to phenylate the primary amine itself by this new method. Two years more and by heating equal molecules of aniline and aniline hydrochloride in the autoclave, Girard and de Laire obtained diphenylamine as an industrial product. In a similar way the homologues were prepared (E. P. 1866 No. 1093).

The next thought was to produce the phenylated rosaniline

from a mixture of diphenylamine and its homologues, analogous to the formation of Rosaniline.   Although this did not succeed, one soon found (*Girard and de Laire* 1866, *E. P. No.* 2686) in consideration of earlier hints on the formation of Rosaniline and Rosolic Acid from pure aniline or phenol and compounds of the fatty series—a synthetic process for the conversion of diphenyl-amine into the sought for blue dyes.   Oxalic acid proved here also the suitable agent.   For some time Diphenylamine Blue was followed by hexanitrodiphenylamine, the yellow coloured 'Aurantia' and after a decade with the beginning of the modern azodye industry, by the valuable Diphenylamine Orange, later by the isomeric Metanil Yellow, the Azoflavine and other dyestuff derivatives.   Also the methylated diphenylamine found application in the synthesis of rosaniline derivatives.   In recent times the diphenylamine is however, not of a small theoretical and practical importance for the knowledge of constitution or the synthesis of important groups of the related dyestuffs.

However let us return to Iodine Violet.

The quickly rising price of iodine through the new demands (*Hofmann, Report on the development of chemical industry* 1875, *I,* 136) was further increased by the simultaneous increase of the Strassfurt potash-salt industry at the cost of the sea weed ashes.   Hence the preparation of dyestuffs, costly in itself—in 1867 a kg cost 160 marks—soon drove to experiments in another direction.   As early as 1861 Charles Lauth, (*Report, Chem, Appl.* 1861, 345, *E. Kopp*) a prominent promoter of the coal-tar colour industry, had observed by oxidation experiments with Hofmann's methylamine, known since 1849, the appearance of violet, light-unfast colours.   Though quite unpromising in the beginning, these dyestuff reactions had attained new interest now.   The explanation of the process of formation of Rosaniline by Hofmann, had in the meantime widened the circle of ideas.   Through the Iodine Violet, the prejudice was removed that the methyl radical must be excluded in the production of artificial dyes. (*E. Kopp. l.c.* 347).   So one asked: Why should one first oxidize the mixture of aniline and toluidine and then methylate? Could not the operation be inverted, first to methylate and then to oxidize?

4

This was the industrialist's simple way of thinking. Where-from to get the alkylated amines without again taking refuge to methyl iodide?

The French industry soon gave the expected answer to this question. Already in 1852 Berthelot had proved the formation of methyl and ethylamine by heating ammonium chloride with methyl or ethyl alcohol at 300-400°C. This scientific hint now led Charles Bardy, the chemist of the factory of Poirrier & Chappat in St. Denis, to the lucky idea of replacing ammonia by aniline in Berthelot's reaction. The pressure-tube-experiment succeeded—aniline was methylated to the dimethylaniline.

Soon Lauth also found out a series of new oxidation methods for the production of dyestuffs. With courage and perseverance Poirrier and Bardy overcame the great technical difficulties of the first dimethylaniline manufacture. They were not afraid of an operation unknown then, high temperature, pressure of 50 atmospheres and above and the corrosive action of the dissociated aniline hydrochloride. Mechanics supplied them with pear-shaped cast iron bombs of an enormous strength of their walls, made from bubble-free metal and the inside protected by acid proof enamels. However still unexplained! Only the tertiary amine obtained from pure aniline is applicable (*Lauth Ber.* 6, 677).

At the Paris World Exhibition in 1867 visitors looked admiringly at a mighty block of "Violet de Paris" with metallic lustre, and besides this at huge quantities of the new intermediate products of industry—the mehylated and ethylated aniline.

A few years later the mystery of this new manufacture was also unveiled. Everywhere begins the successful fight of Methyl Violet and its derivatives discovered in the meantime; the Benzyl Violet, blued by benzyl chloride and of the 'Methyl Green' prepared at first with methyl iodide then with methyl nitrate and finally with methyl chloride, against Hofmann's Iodine Violet and its ammonium base, the Iodine Green which attained a short but splendid life (*Hofmann and Girard Ber*, 2, 440); a fight, the decision of which Hofmann himself furthered powerfully by his detailed communications (*Hofmann, Ber.* 6, 352) on the violet derivatives of methylaniline and by his repeated

investigations on the course of alkylation of aniline and its homologues (*Hofmann and Martius, Ber.* 4, 742; 6, 345; *Hofmann, Ber.* 5, 704, 720; 7, 523, 526; 8, 61, 10, 588, 591).

Also these investigations were conducted in collaboration with the friendly industrialists and dye technicians; on German soil grown, their results entered immediately fructifying the German workshops. So, one attained not only a clear insight into the conditions of formation of the mono and dialkylamines, into the methods of their separation and analytical estimation, into the nature of their higher boiling or non-volatile by-products, but through the study of the latter succeeded also further to the astonishing discovery of a new method of preparation of the aniline homologues. At high temperature the alkyl wanders from the amino or the ammonium group into the benzene ring at an unoccupied para or ortho position. (*Limpach, Ber.* 21, 640, 643). From the quaternium base the tertiary, secondary and primary amines are formed step by step. Yet, it does not require the separated representation of these intermediate steps to bring the operation into practice; it suffices the sufficiently long and strong heating of the hydrochlorides of the primary base with the alcohols concerned in the autoclave.

This is the previously mentioned Hofmann's "method of the wandering of the atom in the molecule." Already in 1878 it became of practical significance for the preparation of scarlet red azodyes from higher homologues obtained ·by the introduction of methyl and ethyl groups in aniline, toluidine and xylidine (*Meister, Lucius & Brüning (H. Baum) D. R. P. No.* 3229). In particular the technical interest was aroused by the valuable pseudo-cumidine obtained from xylidine and methyl alcohol. [*Act. Ges. f. Anilinf. Berlin*, 1882, *D. R. P. No.* 22265 (*Martius*) ; *Hofmann, Ber.* 15, 2895].

Soon after the commencement of these investigations, Hofmann marked the previous gap between science and industry with these words: "When I discovered methyl aniline more than 20 years ago, I never expected that this substance would once become the source of a roaring business." Now, after the quick introduction of his new method into practice, his utterance (*Hofmann, Ber.* 13, 1729): "The industry to-day does not

leave scientific investigations long unexploited," was truly characteristic of the revolution which had occurred since the first appearance of aniline dyes. In fact when one meets the practical results of the latest theoretical investigation in the present patent literature, one is surprised to think that had it been the earlier days the idea of its future industrial utilization must have remained in most cases a beautiful scientific dream only.

Hofmann's method of alkylation in its original and its technically modified form has nevertheless become an imperishable possession of the industry. Although for a long time Iodine Violet and Iodine Green roused only reminiscences of their brilliant past yet one cannot dispense with the co-operation of halogen alkyls for the preparation of other methylated, ethylated and benzylated dyestuffs. Fuchsine was converted into red, violet and their sulphonic acids. One still benzylates Methylviolet. Of the alkali sensitive azodye combinations of phenol, its instability is removed by etherification. One produces Chrysophenine, Congo Orange, Diamine Yellow and Scarlet, or imparts Dehydrothiotoludine the colouring properties of Thioflavine and so forth. However, the methods of alkylation find their principal application in the domain of intermediate products, *e.g.,* one benzylates the secondary methyl and ethylanilines for the synthesis of violet and green acid dyestuffs. in which the benzyl group becomes the carrier of the sulpho group. From o-nitrophenol one prepares its methyl ether and from that anisidine or dianisidine, ethylates metanil for the 'Rhodamine' and 'Nile Blue' producing diethyl meta-aminophenol. Nevertheless all these and many other applications of the method are still surpassed with regard to industrial importance by the manufacture of dimethyl aniline, to whose direct conversion into the approved Methyl Violet numerous large scale uses have joined. Its nitroso derivative is the starting material for Methylene Blue and a series of important dyestuffs; from its ketone, (*the tetramethyl diaminobenzophenone*) has been built Auramine, Crystal Violet, Victoria Blue and other phosgene dyes, while with benzaldehyde and its derivatives it condenses into the leuco bases of green and blue dyestuffs. To a small amount diethylaniline participates in these applications. Other homologues have been likewise produced and ardently searched

for, principally for the purpose of the securing of patents and evasion, but scarcely with any noteworthy practical exception they have found entrance into the text books and patent literature only. Also Bardy's methods of operation has not really been modified. In many factories hydrochloric acid has been replaced by sulphuric acid, the direct application of gaseous or liquid methyl chloride could not any more be displaced by it. Its former dangers have disappeared.

On the artificial preparation of healing agents also Hofmann's method of alkylation has exercised its influence. Starting from the idea (*now going out of date*) that in quinine and cinchonine there is a hydroquinoline residue with methylated nitrogen, one succeeded in the synthesis of Kairoline, of Kairine and finally of Antipyrine. But thallin and phenacetine became the carriers of methoxy and ethoxy groups, and the latter the acetyl phenetidine—owed its origin to the accidental discovery of the antipyretic property of the acetanilide. Immediately with this discovery the speculations on the relationship between chemical constitution and therapeutic activity began to be anticipated. In a similar way one already believed to have found out from the still insecure observation on the alkylated Rosaniline (*Emil Kopp. loc. cit.*) the casual relation between constitution and colour. However, in spite of the rich store of facts one could even here not rely on any exact law. The time has not yet come which will affirm Hofmann's question on the occasion of the discovery of the Iodine Violet. (*Hofmann's Proc. Roy. Soc. loc. cit.*).

"Will not chemistry teach us finally to build systematically the dyestuff molecules whose particular colour-tone we can predict with the same degree of exactitude with which at present we can determine in advance the boiling point and other physical properties of the substances from our theoretical conceptions?"

Chlorination Department :

In the next department chlorination is carried out. We see how by the introduction of chlorine in boiling toluene benzyl, benzal and benzotrichloride are produced in succession.

"This method"—the guide says—"*Beilstein* has taught us in 1866 (*Beilstein & Geitner Ann. d. Chem.* 132, 331; *Beilstein & Kuhlberg, do.* 146, 322, 330). Previous investigations by Deville, Cannizaro, Cahours, Naquet, Limpricht and others had brought to light starting partly from toluene and partly from benzoyl compounds a series of chlorinated derivatives of toluene and their often mysteriously contradictory behaviours. With this state of affairs the industry could not do anything, so far Kekulé's theory was missing and the knowledge that chlorine on toluene behaves quite differently according to whether one lets it work in hot' or cold, with or without an additional chlorine carrier." (*Hugo Müller,* (1862) *Chem. News* 5, 52). Without this knowledge, we would have unknowingly added chlorine in wrong positions in the benzene nucleus instead in the methyl side-chain.   However, that our toluene is a methyl benzene we learnt already from Tollen's and Fittig's synthesis. It was the aurora before daybreak of the benzene theory; in its light we looked for the first time into the nature of homology of our benzene hydrocarbons and searched for the significance of its methyl residue for the process of formation of the Rosaniline.

First benzyl chloride found its way into industry as an alkylating agent. Early one tried also its introduction into artificial bitter almond oil for the perfumery (*Lauth & Grimaux* 1866, *Ann. d. Chem.* 143, 79). But only with the industrial preparation of benzotrichloride for Doebner's Malachite Green, the successful rival of the Methyl Green a new progress set in in 1878. (*Act. Ges. f. Anilinf. Berlin D. R. P.* (1878) *No.* 4322; *Martius, Chem. Ind.* 1879, 81).

Soon the industry succeeded in bringing forward the production of this dyestuff from a leucobase, a condensation product of dimethyl aniline and bitter almond oil, discovered by Otto Fischer, through a suitably conducted method of oxidation. [*Bad. Anil. und Sodafabr.* (*H. Caro*) 1878, *Ber.* 12, 796; *Otto Fischer* 1877, *Ber.* 10, 1624)].

Immediately also the industrial method was found for the preparation of benzaldehyde. One only had at first to fall back on the long forgotten experiments of Cahours and Limpricht [*Cahours, Ann. d. Chem: Suppl.* 257 (1863) ; *Limpricht Ann. d.*

Chem. 139, 319)] to produce again pure benzal chloride from pure benzaldehyde and to heat this in a pressure tube with water. The experiment taught—in confirmation of Cahour's statement that the retrogressive formation took place quantitatively. The preparation of pure benzalchloride from toluene according to Beilstein's prescriptions could not however, meet with difficulties any more (*Cahours loc. cit.* 306).

So the once so costly bitter almond oil was obtained for the industry as a cheap and in many ways useful intermediate product in spite of some loudly expressed doubts. (*Chem. Ind.* 1879, 83). On a large scale benzalchloride was heated with milk of lime in a pressure vessel. As by-product one obtained from benzotrichloride present in the .crude dichloride benzoic acid, which is needed for the aniline blue process and later on for the synthesis of mordant dyeing anthraquinone and oxyketone dyestuffs. However, for this acid, also the process of its direct preparation from toluene by oxidation had been obtained by the industry. (*Fittig, Ann. d. Chem.* 120, 214). Furthermore, with benzoic acid an industrial future opened up for benzoyl chloride and its derivatives.

Already before the discovery of Malachite Green an endless vista of the groups of dyestuffs which can be prepared synthetically had been opened through the works of Baeyer and his students, Emil and Otto Fischer. From the Phthaleins one had reached the domain of Rosaniline. Along with numerous green, blue and violet derivatives of triphenylmethane, the long looked for industrial synthesis of Fuchsine appeared in the attainable distance. Soon the artificial Indigo followed. These were questions of life and death for the dyestuff industry. Industry took an intense interest on the scientific movement and supported it in true comradeship. In the laboratories of the Universities and industries people worked with benzaldehyde, benzyl, benzoyl and benzotrichloride or with their nitrated, aminated and chlorinated derivatives; they were condensed with homologues and analogues of dimethylaniline; and Brilliant Green, Acid Green and Acid Violet were prepared. For the fuchsine process one tried to obtain in a smooth way the reaction which was produced in the melt under side-reactions of the oxidising methyl group

of the paratoluidine by the application of paranitro, paraamino
and paranitrated derivatives ready for condensation. For the
preparation of these agents one used partly known methods and
partly new ones were discovered. For the synthesis of Indigo,
however, one was preparing cinnamic acid from benzal chloride
[*Bad. Anilin & Sodafabr. (H. Caro*) 1880 *D. R. P.* 17467] and
was devising methods for obtaining orthonitrobenzaldehyde and
their related compounds acting likewise. The scientific gain from
these works was great—its influence on the development of the
colour chemistry was also lasting. But small was the amount of
its immediate practical results. Neither the old fuchsine process
nor the natural Indigo was displaced. Valuable green and violet
dyestuffs resulted from them but only in recent times the
originally unobserved condensation of metanitrobenzaldehyde and
its amino and oxyderivatives in the beautiful group of patent
blues attained industrial importance. [*Hochster Farbwerke
(Hermann*) 1888, *D. R. P.* 46384)].

Further applications of the methods of chlorination appeared
in the manufacture of dichloroanthracene (*Cf. Perkin: History
of Alizarine l.c.* 16) for the use of the alizarine industry, in the
preparation of phosgene according to the method of Paterno
(*Paterno, Ber.* 11, 1838), or in the chlorination of naphthalene
and phthalic acid for the production of chlorinated phthalic acids
for Eosine. Also phthalic acid itself was—as we hear—formerly
manufactured exclusively from naphthalene tetrachloride accord-
ing to the old methods of Laurent and Depouilly (*P & E
Depouilly, Ann. d. Chem.* 137, 373). But later the direct
method of oxidation of naphthalene has as well been developed
(*Lossen, Ann. d. Chem.* 144, 71).

We left the chlorination department. In continuation we
were shown the helping manufactures of alkyliodides and the
frequently used ethyl bromide as well as the only occasionally
practised bromination of orthonitro cinnamic acid for the small
but remaining requirement for orthonitrophenylpropiolic acid.
Bromine is mainly used in the eosine dye department. Another
glance at the glittering sublimation chambers of the phthalic anhy-
dride and benzoic acid and we rush through the spacious manufac-
turing halls of the anthaquinone looking at its often described

preparation according to the oxidation method of Graebe and Liebermann, at its still approved purification with sulphuric acid and at the final regeneration of the chrome liquors. A series of simple but big and truly industrial-scale operations! Next we turn to a group of buildings the extensiveness of which already attracted our attention from a distance.

Sulphonation :

Here, we see in long lines, cast iron stirring vessels of the same shape—some bigger, some smaller, provided with heating and cooling arrangements; everywhere are lead lined cisterns, milk of lime, ice, filter presses, evaporating and drying pans, sulphuric acid carboys, iron flasks and tip boxes with oleum and anhydride.

"This is the province of the sulphonation method"—was the explanation. "Here, one adds the sulpho groups, once, twice, thrice, partly retaining them for the later synthesis of water soluble 'acid dyes' partly labile for the purpose of their later replacement by hydroxyl or nitro groups. Mostly it is the matter of the preparation of uniform isomers. On the purity and reliability of these intermediate products depends, as a rule the success of their further consumption. For this the choice of the right kind of raw material, whether and in which position previously substituted or not, the careful adherance to the conditions of operation—chiefly the temperature and duration of action the concentration and amount of acid the application of the methods of exact separation and purification are the deciding facors.

Also in the field of the modern coal-tar colour industry sulphuric acid has proved to be the old friend of the dyer. As one hundred years ago it had found its way into the dye-industry in the stone-ware jars of the 'Nordhäuser Vitriol' to make Indigo soluble, so it performed later, although in a milder form, the similar service to Aniline Blue and Induline which are replacing Indigo. But only in the preparation of sulphonated intermediate products it unfolded its full activity. Science had prepared the field. Numerous conjugated (gepaarte) sulphuric acids had been discovered and had become the support of theoretical concep-

tions. Kekule's theory explained the constitution of aromatic
sulphonic acids, calculated the number of possible isomers, ordered
the known ones, connected them with members of other groups
through transitions, indicated the existing gaps and discovered
methods to fill them.   From the benzene compounds the enlighten-
ment   proceeded   to   the   more   rich-membered   province   of
naphthalene.   Here indeed sulphuric acid has found its many
sided applications. The history of the sulphonated derivatives
of naphthalene, naphthol and naphthylamine, of the aminonaph-
thol and dioxynaphthalene is at the same time the history of the
modern azodyestuff industry.   And this industry which has
already taken over about 70 of the naphthalene derivatives—of
which many are of high, industrial importance—has also called to
life the preparation of aminated sulphonic acids from the series
of diphenyl benzene and stilbene. Yet it was not in this field of
dyestuff that the sulphonated intermediate products attained their
first industral utilization.

In 1867 Kekule had hardly (*Kekulé, Zeitschr. f. Chem.* 1867,
197) declared in a decisive manner Laurent's old phenyl sulphonic
acid for a phenol sulphonic acid, in contrast to its former idea
as ether, acid by proving its existence in two isomeric modifica-
tions and whose methyl and ethyl ether he prepared, when he
also taught the exchange of the sulpho group by the hydroxyl
group in the potash fusion. (*Kekulé loc. cit.* 300). Out of
Mitscherlich's benzene sulphonic acid originated the synthetic
phenol and from the isomeric phenol sulphonic acids—catechol
and resorcin.

Two years later Graebe and Liebermann obtained artificial
Alizarine by the potash-fusion of the dibromo-anthraquinone.
Here bromine was replaced by the hydroxyl group. The next
assumption was; therefore, to replace the costly bromine by
sulphuric acid.   But Anderson, the discoverer of Laurent's
anthraquinone (*Anderson, Ann. d. Chem.* 122, 302) had already
observed its stability by heating it with sulphuric acid. Experi-
ments within the usual sulphonation limits confirmed his data.
Yet all the testing technique goes far beyond those limits, it
heats just up to the boiling point of sulphuric acid and attains
the expected sulphonic acid of the anthraquinone.   Further

experiments show that the reaction temperature can be lowered by the application of fuming sulphuric acid according to the anhydride-content of the acid. Thereby the side reactions are avoided as far as possible. Yet at that time acids rich in anhydride were not in the market. In 1874 one had to prepare them by distilling 'Nordhäuser Vitriol' but later Johann David Starck prepared them in Bohemia and shortly afterwards Clemens Winkler presented the industry with the synthetic method of preparation of sulphuric acid anhydride.

In possession of all the helping agents from monohydrate to the pyrosulphuric acid and the anhydride, the sulphonation technique has now assumed an unprecedented precision. Better than previously one can check the conditions of reactions for the best possible production of the monosulphonic acid of anthraquinone for the 'blue tinted' Alizarine, and of the two disulphonic acids for the yellow-tinted flavo and anthrapurpurine respectively. The earlier discovered methods of separation of the sodium salts were improved, their preparation from the calcium salts had experienced commercial development already at the beginning of this industry.

The artificial Alizarine remained the school and pattern for the later handling of the methods of sulphonation. Very little was added. One learnt to sulphonate some bases by transposition of their acid sulphates in roast processes (*Nevile & Winther, Ber.* 13, 1940), in some cases the precipitation and separation of sulphonic acids were simplified by precipitation of the crude fusion products with common salt, or in other cases the harmful admixtures of isomers were removed by fractional precipitation with diazo compounds, through spirit-separation and in other ways. Also one penetrated into the nature of sulphonation, and considered the hydrolytic action of the progressive dilution. In recent times one succeeded in the field of anthraquinone, to put under the sway of a fruitful principal reaction the energy of oxidation of the anhydride manifested in the side reactions. The first technical fruit was the Alizarin Green [*Bad. Anil. u. Sodaf.* 1888 *D. R. P.* 46654 (*Rene Bohn*) *Graebe Ber.* 23, 3739]. An abundance of analogous applications of this "Bohn's Reaction" followed afterwards.

Early one also had observed and utilized the replacement of sulpho groups by nitro groups. An improved method of picric acid preparation was founded on the nitration of phenol sulphonic acid (*Schmitt & Glutz,* 1869, *Ber.* **2**, 52) and led immediately to the similar production of dinitronaphthol from the sulphonic acid of ᴀ-naphthol which in the meantime had been discovered (*Darmslädter & Wichelhaus, Ber,* **2**, 113; *Schaeffer, Ber.* **2**, 93). Ten years later it was found that besides the labile sulpho groups also immobile sulpho groups, stable to nitration may be introduced into ᴀ-naphthol by increasing the energy of sulphonation. Thus one attained the dinitronaphthol sulphonic acid (*Bad. Anil u. Sodaf.* 1879 *D. R. P.* 10785; *H. Caro*), the Naphthol Yellow S, our most approved nitro-dyestuff. We follow the sulphonic acids on their way to the alkali fusion.

Alkali Fusion :

In the far stretching working halls one sees firing arrangements for fusion operations, for heating the open cast iron, and closed wrought iron melting pots, the latter of boiler form and provided with horizontal stirring arrangements. There one melts with caustic soda—the pyrometer showng up to 300°C and above, here one heats and melts under pressure with strong caustic soda solution. Everywhere are pans for solution, pressure vessels, precipitation vats with slits for the outlet of sulphurous acid, extraction and distillation apparatus.

"Here reigns"—says the guide—"Kekule's method for the conversion of aromatic hydrocarbons to phenol. Almost each of its applications marks a new section in the development of our industry. As is known, this classical method was published simultaneously by Kekulé, Wurtz and Dusart in 1867, a coincidence which has repeated itself several times in the history of discoveries. (*Zeitschr. f. Chemie* 1867, 299-301). Through the potash fusion of benzene sulphonic acid discovered by Mitscherlich in 1834, Kekulé and Wurtz obtained the first synthetic phenol. Wurtz also obtained from Deville's toluene sulphonic acid the homologue, cresol and from Faraday's naphthalene sulphonic acid, the naphthol.

Dusart, however, for the first time fused an isomer of the

disulphonic acid of naphthalene previously obtained by Berzelius and Laurent, and showed the way how to obtain a dioxy-naphthalene. In the meantime Kekulé however, took a further step forward and taught the applicability of the method on the phenol sulphonic acids.

Hardly had this method been known, when it found entrance into the industry. Its first appearance on the stage of industry in 1869 was at the same time its most successful performance: it was the preparation of Alizarine from the sulphonic acid of anthraquinone. But what an amount of work had to be spent before one succeeded to obtain a clear view into the nature of these sulpho acids and into the particular conditions of its fusion to follow its conversion by non-colouring oxyanthraquinone and other intermediate products into the much sought for dyestuffs, and to establish the nature of the processes of oxidation and reduction which played here a prominent role! A hard struggle for competition, to which many had to succumb spurred on to restless activity. One heated in rotating drums, in double jacketed pans, in a baking oven, applied superheated steam, air, oil and phenanthrene baths.

And when finally one again fell back on the pressure melting, which had been approved of already at the beginning of this industry, but adding the potash chlorate to the caustic soda and introducing mechanical stirring then only the fusion process attained its practical conclusion. The years of apprenticeship were overcome. One had learnt the handling of the method in all possible directions. This knowledge proved good to resorcin first. Eosine was discovered in 1874. For its first preparation served a costly laboratory preparation. The resorcin of Halsiwetz and Barth (*Ann. d. Chem.* (1864) 130, 354) was produced by the potash fusion of the galbanum resin. This was its usual methol of preparation in those days. For the industry it had no prospects. But the projection of Kekule's theory, the works in the fields of stereo and structural chemistry, had already brought to light other methods, including potash fusion of the old benzene disulphonic acid of Hofmann and Buckton (*Hofmann & Buckton, Proc. Roy. Soc.* 1856, 8, 162). Quickly the technical difficulties of its conversion into the commercial

scale were overcome and resorcin became the starting material for the new branch of industry of " Resorcin Dyes."

Three years later, and we consult the works of Wickelhaus and his school from the year 1869 (*Ann. d. Chem.* 152, (*Eller*) 275; *Schäffer*, 279). The time of the naphthol dyes had come. Formerly one had already prepared small quantities of *α*-maphthol for its dinitro dyestuff. Now one required both the isomers for the mightily developing industry of the azodye-stuffs, above all of *β*-naphthol. All preliminary conditions for an unhindered production of the *β*-naphthol were given. For the individual preparation of the corresponding naphthalene sulphonic acids and the separation of their calcium salts there were already exact directions in existence. One has become the master of the caustic soda fusion (*Ber.* 3, 195, 710). So one has only to develop the technical side of the industry.

In the suite of the naphthols appeared soon their mono, di- and tri- sulphonic acids. One turned to their investigation, sought and found new isomers and utilized the important observation, that the *β*-naphthalene disulphonic acid (*Ebert and Merz, Ber.* 3, 611) in the potash fusion replaces easily only one of its sulpho groups by the hydroxyl group. It was now found that by careful fusion in the *α*-naphthalene disulphonic acid also the reaction can be arrested half way. The sulphonic acid thus obtained (*Cassella & Co.* 1888, *D. R. P.* 42112) can be further sulphonated or can be converted into *β*-naphthyl-aminosulphonic acid by heating with ammonia. Naphthalene trisulphonic acid had previously shown a similar behaviour (*Gurke & Rudolph*, 1885, *D. R. P.* 38281).

Step by step, first one, then the second sulpho group could be replaced. In this way one obtained a naphthol disulphonic acid and then a dioxynaphthalene monosulphonic acid. Now di- and trisulphonic acids of *β*-naphthol also were subjected to a similar treatment. Dioxy naphthalene mono and disulphonic acids were formed. The partial caustic soda fusion proved an important auxiliary means for the preparation of sulphonated oxy-dioxy and aminonaphthalene, of which some have attained a considerable technical significance in the azodyestuff industry.

In 1887 the Phthaleins of the metaaminophenol were dis-

covered.   Rhodamine,   the   derivative   of   the   diethylated
metaaminophenol, appeared as its first representative in the
market.   For the preparation of its basic raw material a method
had been employed which was up to then not used : caustic soda
fusion of an amino sulphonic acid.   From metanilic acid was
derived the meta-aminophenol, from the alkylated amino-
sulphonic acid the corresponding alkylated product.

Very soon this reaction was transferred to the naphthalene
series and from napthylamine were obtained mono-,di-, and trisul-
phonic acids, new aninonaphthols or their mono and disulphonic
acids—intermediate products which by the combined action of its
oxy and amino groups proved themselves particularly suitable for
the synthesis of peculiar azodyestuffs.   Still, every amino group
cannot withstand potash fusion and not every sulphonic acid group
can be attacked.   By the same treatment of Piria's naphthionic
acid—the most important naphthylamino sulphonic acid of the
industry—the frequently used α-naphthol sulphonic acid of Nevile
and Winther resulted.

This acid had broken the previous prejudice that only the
β -naphthol and its sulpho acids are capable of producing the
beautiful acid-fast azo-dyes.   It is formed by the direct sulpho-
nation of α-naphthol together with its isomer, the first α-naph-
thol sulphonic acid of Schäffer.   Yet its quantity is too small and
its separation too difficult.   Every admixture of isomeric acids
dulls the colour.   Hence, it was prepared at first according to the
process of Nevile and Winther, from naphthionic acid by the
method of Peter Griess.   Even now-a-days this method is in use.
Let us now turn to its consideration.

Diazo Section :

A group of three connected workshops lies before us.
" This is the region of nitrous acid "—says the guide.   " In
the oldest building the diazo compounds of Peter Griess are
prepared in so much as they serve the production of stable inter-
mediate compounds.   With their help one produces aminoazo
compounds, required for the manufacture of Induline, Safranine,
Disazodyestuffs and for other.purposes, or one replaces as already
mentioned the amino groups by hydroxyl groups.   In 1864 this

method found first industrial application in the preparation of aminoazobenzene for the manufacture of the first spirit-soluble Induline. One started from Griess' diazoamino-benzene and converted this into the isomeric aminoazo compound in a manner later explained by Kekule'. At that time the latter had already been brought to the market by Nicholson on an experimental scale under the name of Aniline Yellow. The first formation of this dyestuff has been observed by Mene'. Other methods proposed by Schiff proved useless. [*H. Schiff, Ann. d. Chem. 127, 345*). *The method for the preparation of Aniline Yellow described by Schiff by the action of hydrate of antimony acid and stannic acid 'on aniline depended according to the new experiments of the authors exclusively on the action of the nitrite accompanying the commercial sodium salts of tin and antimony acids.*]   .

However, as dyestuff the aminoazobenzene did not become popular, as little as the aminoazonaphthalene, previously prepared by Perkin and Church. The instability of the first on the dyed fibres hindered its technical use and only in the presence of acids aminoazonaphthalene retained its rich-violet colouration. Already when washed and rinsed it turned to yellowish brown. Other monoaminoazo compounds behaved similarly. But they have become nevertheless important intermediate products. By introducing sulpho groups one has endowed aminoazobenzene with the valuable properties of the "Fast Yellow". The para-diamine produced 'by the reducing fusion of aminoazo compounds were early utilized for the synthesis of the safranine dyes before one became aware of its mode of action. Its diazo compounds led to the group of disazodyes and therewith to a new section in the history of development of the azodye industry. They became the basis for the manufacture of blue and red Indulines of the benzene and naphthalene series.

Of the double decompositions of the diazo compounds with water, alcohol, acids and alkalies, discovered by Griess only the first had attained considerable technical importance. By diazotizing ⍺-naphthylamine and by boiling it in presence of nitrous acid one obtained at first dinitronophthol and in a similar manner from benzidine, the tetranitrated diphenol.

Both the methods have been given up.   But by exclusion of nitrous acid this way has led to important naphthol mono-, di- and trisulphonic acids and to the discovery of the naphthol sulphones and their sulphonic acids.   The industry has understood how to endow these transformations to smooth running operations. With Griess' reaction and the easier replacement of hydrazine group by hydrogen, Science has thrown its bright light on the isomeric relations of our naphthylamine and naphthol sulphonic acids.

The principal field of Griess' diazo compounds is, however, the industry of azodyes.   Owing to its easy decomposition and its capacity for being applied directly without previous separation from its solution it was produced on the place required. Even in the dyeing establishments they are prepared on the fibre and further converted into azodyes.   Our further trip will furnish explanation for this.   In the domain of explosives, which open the paths for peaceful relation, which disclose the treasures of the earth and are ready to protect our highest life-ideals in times of danger, the diazo compounds have not yet found their way in spite of their powerful reactivity.   From the experiments conducted so far the compounds proved to be too easily decomposable.   Yet, the last word cannot yet be pronounced.

From the diazotization section in which we met again with the well known methods of preparation, with their classically simple operating agents—titrated nirite solution, ice, stirring vessels, boiling pans and so on—we entered the next working room where aromatic hydrazines are prepared.   Here for the first time the far-reaching scientific investigations of Emil Fischer were utilized for human amenities (*Emil Fischer, Ann. d. Chem.* 190, 67).   According to the discoverer's method we see here phenylhydrazine on a large scale resulting from its final distillation.   It has found its way into the manufacture of Antipyrene.   Yet the dyestuffs also have not been neglected. We were shown the preparation of phenyl hydrazine sulphonic acid from the sulphanilic acid and heard the explanation how from it by condensation with the dioxytartaric acid the beautiful yellow colouring matter Tartrazine is formed.

5

Nitroso Compounds :

The third section consists of the nitroso department. There Baeyer's aromatic nitroso-compounds are manufactured. An aqueous solution of the nitrite flows into a hydrochloric acid solution of the dimethylaniline, cooled with ice. In a short time the mixture is solidified to a bright yellow crystal-broth. " This is the nitrosodimethylaniline hydrochloride—the oldest and technically the most important representative of the nitroso compounds "—says the guide (*Baeyer & Caro, Ber. 7*, 809, 963). Also its discovery, its scientific significance and utilization represent an example of the intimate reciprocal action of science and practice. Scarcely one year after the discovery of this reactive group by Baeyer and his school—already in 1878—the principal application of nitroso-dimethylaniline in the preparation of Methylene Blue was found. Soon other applications followed, some were of transitory nature while others were of permanent value. By heating nitroso-compounds with metadiamines or by joint oxidation of the latter with paradiamine derived from the nitroso-compound, one obtained red and violet neutral dyes; with ᵦ-naphthol the valuable New Blue was produced and from an indigo-substitute, Indophenol was formed. Of considerable this again a series of other derivatives; while with ᵅ -naphthol technical interest were the mordant dyes—Gallocyanine and its derivatives produced by the action of gallic acid.

On all primary, secondary and tertiary amines and diamines and on phenol and dioxynaphthalene and their sulphonic acids nitroso-compound was brought into reaction, to the same extent as they became accessible and the theoretical explanation of the processes did progress. Many a new azine and oxazine dyestuff appeared in the market.

However, homologous and other nitroso-compounds became also useful intermediate products or found direct entrance into the dye-industry.

From the nitroso derivatives of the alkylated metaamino-phenol one obtained by reciprocal action with ᵅ -naphthylamine the Nile Blue prized for its clear tone. It was discovered that orthonitroso phenol together with iron salts resulted in a stable green, with copper salt in brown, with some other metallic salts

in other coloured compounds which were fixed upon the fibre, and dinitrosoresorcin, nitrodioxy-naphthalene and particularly nitrosonaphthol sulphonic acids were produced.   Also in the dyestuff industry one met with the preparation of the resorcin compounds.

An extension of knowledge and a new impulse to the synthesis of the dyestuffs were brought forward recently by the conversion of the nitrosoamine into the nitrosoderivatives of the secondary aromatic amines, discovered by the combined action of scientific and technical investigations (*O. Fischer & E Hepp, Ber.* 19, 2991, *Ann. d. Chem.* 243, 272*ff.*). Already in the theoretical field and in the course of Victor Meyer's investigations on the hydroxylamine reaction and the constitution of the nitroso compounds the discovered method of the formation of nitroso-phenol (*H. Goldschmidt, Ber.* 17, 21**S**, 2060) by the action of hydroxylamine on the corresponding quinone has led to the conception of these nitroso-compounds as quinone oximes and further, to a modified view of the constitution of these and analogous quinoneimides and groups of dyestuffs derived there-from.

Phenol Carboxylic Acids :

Workshop after workshop! method after method!   Here a glance at the introduction of the carboxyl group into phenol: Kolbe's synthesis of salicylic acid (*Kolbe, D. R. P.* 426), improved by the pressure process of Schmitt (*R. Schmitt,* 1884, *D. R. P.* 29939).   We heard that also for the dyestuff industry this process has become useful since 1884 the first valuable salicylic acid dyestuff has been found in Chrysamine.   Soon other salicylic acid dyestuffs were discovered, dyeing like chrysamine but without the use of mordants or like this, possessed of the capacity to produce fast chrome-lake.   Naturally one attached further interest on the homologous cresotinic acids and on the analogous carboxylic acids of the naphthols.   There one inserts by an indirect method taught by Michler (*Ber.* 9, 400, 716, 1900), a student of Victor Meyer, a carboxyl group into tertiary aromatic amines.   By the action of phosgene at first the acid chloride is formed.   Out of this the acid, the ketone and further

the hydrol are produced.   According to this method ketones are prepared from similar or dissimilar bases.   In the section of phosgene dyes the third amine is added to its methane carbon atom, which transforms it into Auramine, its ketoneimide dyestuff.   ,

Further on, we see the flameless combustion of methyl alcohol to Hofmann's formaldehyde (*Hofmann, Ann. d. Chem.* 1867, 145, 357; *Loew, J. f. prakt. Chem.* 33, 321; *Tollens Ber.* 19, 2133), one of the latest and most welcome acquisitions for the synthetic chemistry.   Scarcely had the aldehyde become accessible for the technique it also entered the service of the dye industry—joined together two molecules of the dialkylated metaaminophenol for the formation of rhodamine like Pyronines, caused a similar formation of diphenylmethane from meta-toluylenediamine for the synthesis of yellow coloured acridine dyes, utilized in the same ways as salicylic acid and its homologues for the preparation of mordant-dyeing carboxyl derivatives of the Rosolic Acid.   However, a still higher goal is just before formaldehyde : the technical synthesis of Fuchsine.

From the anhydroformaldehydeamiline of Tollens (*Tollens, Ber.* 17, 657 ; 18, 3307) the diaminodiphenylmethane results by heating it with aniline and when aniline is substituted by tolui-dine and xylidine a series of homologous bases are obtained. These intermediate products (*Höchster Farbwerke,* 1889 *D.R.P.* 53937) may further be condensed to triphenyl-methane dyes by heating them with aniline or toluidine salts in the oxidation melt. The homologue of *p*-rosaniline produced from diaminoditolyl-methane appears in the market as the New Fuchsine.   Acetal-dehyde also found its application.   The once epochmaking Aldehyde Green belonged already to the past.   In return, quinaldine, formed from aniline and paraaldehyde by Doebner and V. Miller (*Doebner & V. Miller, Ber.* 14, 2812, 15, 3075, 16, 2464)—a result of Hofmann's wandering of atom in the molecule and the quinoline synthesis of Skraup (*Skraup, Ber.* 13, 2086)— became the starting material for the magnificent yellow colouring compound Quinophthalone.

Still the domain of the intermediate products has not yet been traversed—we have so far observed the rules of the most

important working methods only. Yet we have seen sufficiently how out of a few coal distillates the hundred fold nourishment, the life blood of the coal-tar colour industry is derived.

In an unending series, method after method was concluded, new ones joined the old ones, the products of their reaction appeared in endless changing forms, every product being also the basis for an established, improved or new dye manufacture. We recognised the pushing force of the reciprocal action between theory and practice.

Theory and Practice Unite :

During our fleeting walk through the works, the development of the chemistry of aromatic compounds passed our eyes. We heard the celebrated names of its oldest investigators, of their students and their students' students. We saw how the scientific teaching produces inexhaustible successions of generations and how this knowledge has penetrated deeper and deeper into the methods, thought and work of the industry. The oppositions disappeared : the empiricism has grown into science, and science has solved practical problems. In the field of the intermediate products manifold and intimate contact between theory and practice took place. The aromatic compounds enter immediately the industrial life, the new reaction becomes the industrial process, the laboratory preparation in no time—the commercial product. The experienced eye of the technician is needed not for their discovery but only for the knowledge of their practical value. On the extension of this field the whole scientific chemistry works in the scientific laboratories of colleges and factories.

Therefore this field must extend itself incessantly. New methods, new products must come out of scientific work. A stagnation is no longer possible. The first duty of the industry is to keep here in touch with it. The times of the ' old experts ' is long over. However with the expansion of the field of intermediate products its independent structure, its emancipation from the special province of the dyestuffs, drugs, luxury products and explosives will progress. The patents are extinct, applications do multiply. The best conditions for production and sale prevail. But primarily the development of the big chemical

industry and of transport conditions are the deciding factors. One cannot deny the impression, that in foreign countries also and specially in England, a further progress in this direction will badly affect the German intermediate product industry.

Let us therefore, take care of our auxiliary industries and let us maintain the scientific priority attained since Kekule's teaching. Let us in the restless change of theory and practice always add new intermediates, always new and fresh life blood to the mighty body of the German dyestuffs industry.

This central group was called rightly by the guide: The heart of the industry. '

We now turn to the dyestuff departments. Before that we can just cast a glance on the administration rooms and the laboratories of this group.

Executive Section :

It is an imposing building which we enter. In the numerous offices of the individual leaders of industry are accounting and filing. Clearly arranged manufacturing tables give a daily progressing picture of the production of each industry. Not as it was formerly the custom in chemical industries and chiefly in England, under the management of uneducated foremen, that knowledge of the manufacture rests more on estimation or on the average results of longer period, on strict business principles considering even the smallest instead, the calculation of cost price is determined. One can exactly recognize where the firm stands, where it fails, where it can be improved and where to economize. The daily figures speak for themselves. Every firm fights for its existence and competes with the others. In this way success cannot fail.

Factory Laboratories :

The bright and elegant laboratories furnish an impression of scientific research institution, only everything is more spacious than in the colleges—so arranged as to deal efficiently with the immense amount of work done at the same time. Nothing is missing of the latest apparatus of the chemical and physical

laboratory techniques. Here new products are prepared in perfectly pure condition, there they are analysed or their physical constants are determined. One investigates the purity and the content of the materials and manufacture, investigates the utilization of the by-products or by improving methods of preparation works according to patent literature and pursues the progress of the competition by testing their market products. The methods of investigation furnish a true picture of the technical use. One prepares the dyestuff and dyes. Attached to the halls is a "technical laboratory", a factory in miniature, with mechanised working contrivance and apparatus to the pattern of industry. Here methods are at first tried on a bigger scale.

At the view of those splendid auxiliary means of the modern dyestuff industry we thought of the scanty factory laboratories of the by-gone days.

Struggling Period :

"And yet", the guide says—"we have grown into the present mighty position from such small and poor beginning. No gold-bearing monopoly stood at the cradle of the German industry. There was no German Empire and no German patent right. Enterprise and capital were lacking. One mistrusted one's own power and imitated foreign discoveries; England and France were closed to the market by patents, only timidly and unprotected we ventured into the world market. The German industry was still unnoticed in distant countries, at home its unfolding was hindered by the disruption of the States; there was no uniformity in law, coins, measure and weight, communications were difficult and undeveloped, our industries were dependent on raw materials, machinery and foreign products, our mining and textile industry were in its first stage of development. Still the German Federal States under-estimated the powerful economic impetus of the chemical knowledge which scattered its isolated rays from the narrow laboratories of Liebig, Wöhler, Kolbe and Bunsen. Liebig's flaming words (*Justus von Liebig's Lectures and Treatieses ; by M. Carriere* Pp. 7) "The conditions of chemistry in Prussia were not taken to heart, the great centres of learning at Bonn and Berlin were still waiting for their brilliant

resurrection. In England Hofmann was working as the intellectual centre of the industry, Kekule established his school at Ghent, we had to learn the first information of his new teaching in a foreign language and writing (*Kekule, Bull. Soc. Chem. Paris* 1865, 1, 98) and in the laboratories · and workshops of foreign countries were the later founders, directors and advisers of our big works."

Thus we took up the battle of industry on a narrow field with feeble material and spiritual weapons, cautiously and hesitatingly. The free competition was our spur. One had to fight hard for one's own existence to exploit oneself new discoveries, courage and protection were lacking. One took the safer and easier course. "At first one ascertained the demand for the new products imported from foreign countries and acquaint oneself most accurately with the requirements of the market. One travelled personally, tested, mixed, dyed, taught the dyer and found out new applications. Then one chose amongst the most approved of foreign patents and began their own manufacture. But one worked hard, thoroughly and conscientiously, improved and economized from the first hour onwards, contented oneself with modest profit, while in the countries which enjoyed the monopoly, gold streams rained, and only the ready profit, scarcely yet the production cost and safe future were considered any more there. *The watchword of the German industry became cheap and good ! Character and education of the German manufacturers came to be regarded as principal assets.*

Soon however, the French monopoly on Fuchsine and its application hindered the free development of the dyestuff industry there, and deluded in the dreamed safety of the patent, one looked indifferently at the industrious German neighbour. In England the Fuchsine patent fell and the market became free. The leaders of the English dye industry retired from the scene of their activity, there were no youthful successors of equal rank. Hofmann returned to Germany. So our German industry emerged from a poor beginning, it had to experience serious and anxious time. The work has, however, strengthened its power, and science was its true support.

And as afterwards the great time for the German victories came and after them the rise of the German Empire, then also the industry found on the battle-field what it still lacked: self-reliance and the consciousness of its own strength. Everywhere, a new enterprising spirit was to be noticed, capital turned to chemical industries, great firms and companies came into existence. German discoverers came forward; in the first line being the artificial Alizarine. Soon, the influence of the German patents became obvious. Its first command was: *You should not imitate ! Find yourself !*

As we have unfolded the wings of our own spirit we hastened ahead every other country on the path of discoveries. So was not the rise of the German Empire and of the German dye-stuff industry an accidental, timely coincidence?

Look around! See the growth of our cities, the mighty developments of the entire German industry. Out of this frame you cannot take away the picture of our branch. It is—as everything—a child of its great time.

We enter an extensive factory yard. At the centre is situated the central laboratory of the three big dyestuff departments. In front and to the right and left the enlivening main roads of the aniline, anthracene and azodyestuffs departments stretched out to a long distance. At the entrance of each department are the factory laboratories, administration offices and stores.

Storing and Despatching :

A walk through the stores and despatch departments gave us an impressive figure of the many varieties and the world consumption of the dye industry. An incalculable amount of the manufactured and half-finished goods arrive from the factories, almost every dyestuff in the form of different commercial grades, every one suited for its particular use, partly mixtures, partly uniform, partly of homologous, isomeric and analogous series. Here they are sorted, packed to be sent in barrels, boxes and chests to their destination. Their addresses and gay coloured labels in every language—amongst them many an artistic creation of exotic imagination—indicates where they go to, what they

dye, how they are called in commerce, and that they enjoy as German discoveries the patent protection of home and abroad. Everywhere the esteemed trade mark—" German Tar Product Industry." Under this mark German chemistry carries its name into the workshops of the home trade and across the seas and caravan routes, to the most distant habitations of human culture. Even in the homeland of indigo and wood dyes it teaches the simple use of the artificial products to the age-old technique.

Here, the importance of the patent and trade mark protection for the development of our national coal-tar colour industry appears visible. The German goods no longer hide their origin under degrading foreign trade marks. *For, only the work of imitation dreads the light.* These times—we feel it here, in view of the world conquering activity under our own flag—can and must never return for Germany.

How long can the related Switzerland fail to appreciate the ennobling influence of the chemical patent?

Nomenclature and Business Policy :

During a closer look at the dyestuffs we are told that hardly ⅕th is used at home, the whole of the remaining goods will be sent beyond the German boundaries. The dyestuffs with their well known brilliant metallic lustre, often brilliantly crystallized, shine forth from all their packing and sorting places, at their naming we hear old and new well sounding trade names—a unique nomenclature, mostly fittingly denoting the dye-character. the method of application or origin of the product, also often reminding one of the timely events connected with the time of discovery, even the red of the battle-field of Magenta and Magdala, and the name of ' Bismarck ' is not forgotten. It may be recalled that Magenta was discovered soon after the battle at Magenta in North Italy in 1859. The major part of the production goes to the establishment of trade, which the industrious German tradesmen finding the field of activity at home too narrow, have established in industrial and commercial centres of foreign countries. To these businessmen, well-versed in the requirements and laws of their countries, to the business branches and agencies one owed gratefulness for a great part of the deve-

lopment at home. Besides this also German affiliated industries have been established under the pressure of foreign patent or custom laws in France, Russia and England. There the patents were produced or one finished up the half ready products of the original home-factory for which the duty was much less. Thus the tree of the German industry was to send its roots to distant foreign countries. Was this for the use and advantage of its own development? The future will show. .For the total development of the coaltar colour industry the translation of the German method of work may only be beneficial. This has already been recognized. ,

" The object of our to-day's inspection "—says the guide— " requires no insight into the technical details of the dyestuff processes. Its nature, its results and aims we can learn in the central laboratory lying in front of us."

Central Laboratory :

The director of the laboratory, who received us, conducted us through gorgeous working rooms, in which bands of young investigators, mostly former assistants of our great teachers— were conducting their scientific investigations with visible zeal. We hear that contrary to the factory laboratories, here the entire field of the dyestuffs finds its uniform consideration. One searches for new dyestuffs and processes, follows up new phenomena in the field of literature and discoveries, verifies the observations made in the factories for their full scientific and technical possibilities. In a particular department which works under the guidance of a patent-lawyer, the daily increasing patent literature is worked out and the fight for the protection of the own discovery against unauthorized appropriation and the much more objectionable ' round about way ' is led with a sharp pen and the weapons of the conclusive experiment. These patent controversies are the inveterate enemies of the industry—with the lingering and unsatisfactory fights one dissipates the best energies. Yet one has to put up with them as a necessary evil. For, out of it the discoverer's legitimate right in the peculiarly formed legal domain of the modern chemical industry develops ever so much clearer. For the completion of this branch the

German tar industry together with the German patent office and the Imperial Court of Justice takes the greatest interest.

In the third department of the central laboratory one was engaged in the practical application of the dyes, therefore particularly with dye houses.

"First, however," says the laboratory director—"let us have a glance at the collection of our dyestuffs."

Factory Museum :

We followed him to a museum-hall, filled with big and small glass cupboards. 'In these intermediates and the dyes produced therefrom are exhibited. The most magnificent cupboards announced in letters of gold that they have been awarded with highest prizes and been sent back here from World's and Discoverers' exhibitions.

In one of these glass cupboards richly coloured picture attracted our attention. Series of phials, glass cylinders and basins ascend upwards in terraces. Those at the bottom contain the colourless, crude and intermediate products. From them the ever richer groups of colouring matters and their derivatives develop, like coloured buds and flowers, every series originating from the lower one, every dyestuff with its neighbour above and below, right and left, is inter-connected by chemical transitions. A plastic text book of the colour chemistry! The whole structure is arranged in the three principal groups of the aniline and anthracene dyestuffs, every group again into a more limited family and all these branch out upwards from their mother-substances which are partly colourless and partly coloured. Thus we find in the family of the Fuchsines the colourless triphenyl carbinol; amongst the Alizarine dyes: the pale yellow anthra-quinone; in the azodyes of the benzene series: the yellowish red azobenzene oil; in the naphthalene series the dark red azonaph-thalene. In other families of dyes we meet the diphenylmethane or the benzo and phthalophenone, the diphenylamine and thio-diphenylamine, the acridine, indole, phenazine, diphenylene ketone and a series of other mother-substances. We know that none of them are capable of dyeing, and yet we see that the grouping of their atoms forms the common family character of their

coloured derivatives, which were obtained as a rule by working their salt-forming groups; or to which they were built up again—as this their next derivatives show—in most cases by the addition of oxy or amino groups according to the already familiar methods of the intermediates. In other cases we find, as the next sprouts of the colourless mother-substances a series of colourless leuco compounds·from which only by the removal of water the coloured and colouring dyestuffs come forth.

Thus at first glance we recognize that the extensive field of dyestuffs has been made accessible by a systematic structure of a simple, practical and theoretical view point. The huge growth of the individual phenomenon arrange itself into luminous groups, families and classes, starting from few with regard to their constitution well known substances which can be synthetically prepared, which one may denote as " dye-stuff radicals." The previous empirical division according to the shade of colour, or to the ' acid ' and ' basic ', ' substantive ' and ' adjective ' dyes is pushed in the background as well as every classification according to the number of their carbon atoms. The transformation from colourless into coloured, from the coloured into the colouring condition can be followed, not less than the further change of the colour-tones and the dye character by the entrance of the substituting elements and groups of atoms in fixed number and position.

Considerations obtrude on the relation of the chemical constitution of these classes of compounds with their technically most important properties of the colour and the capacity for colouring.

" This scientific knowledge of the province of dyes "—says our guide—" has led to the present well-planned investigation which is quite different from the empirical test of former times. It is the last and most beautiful result of the combined work of· theory and practice. Let us now see by which way we reached there. At present this exhibition cupboard will remind us of the international competition that has become a mighty agent of progress on our way in spite of how little perhaps some may estimate the gain from a world exhibition. By each of such public tests the emulation was kindled and the reports of the

prize-court, particularly those from the pens of Hofmann, Wurz and Lauth created an imperishable and instructive text books. Let us turn next to the historical compartment of our collection.

From one of the cupboards the director of the laboratory took out a flask with a deep violet liquid. The label turned yellow, ran: " Tyrian Purple. Perkin and Sons, 1857."

" This is "—he says—" our oldest dyestuff in alcoholic solution, in its first commercial form. At the end of 1857 it came into the English market and was named Mauve in the English dyers' circle as it reminded them of the shade of the flower, mallow; on the Continent it was called " Aniline or Perkin's Violet." The statement of this discoverer that it was a commercial necessity was not valid for long. (*W. H. Perkin, Chem. News* 3 (1861), 347). Cheaper and more beautiful dyes have gradually replaced it in its principal applications, although in fastness no other later aniline dye could surpass it. However, this first aniline dye has fulfilled its great pioneering mission, what later was only a natural consequence of its discovery. And this discovery had to open up new paths because as this the history of all great successes has taught—at its birth the rare constellation had prevailed : The right man, in the right place. at the right time.

The man was: William Henry Perkin, the place: The Royal College of Chemistry in London, the time: the year 1856.

On our request to describe more closely the origin of the industry and its founder we were told:

Perkin was—according to Hofmann—the son of an architect. Under the influence of the paternal profession he developed since his early childhood a tendency for practical mechanics. He acquainted himself with the use of the working tools, practised drawing and construction-sketches, prepared models and got familiar with the fundamental teaching of machinery. So, he early acquired a considerable part of the mechanical knowledge and dexterity, which now-a-days are necessary for the training of a factory chemist. The father had hoped to train him as his successor—but just 12 years of age—Perkin took the path in the direction fixed for his life. The accidental sight of chemical experiments inflamed the boy's imagination. He decided to
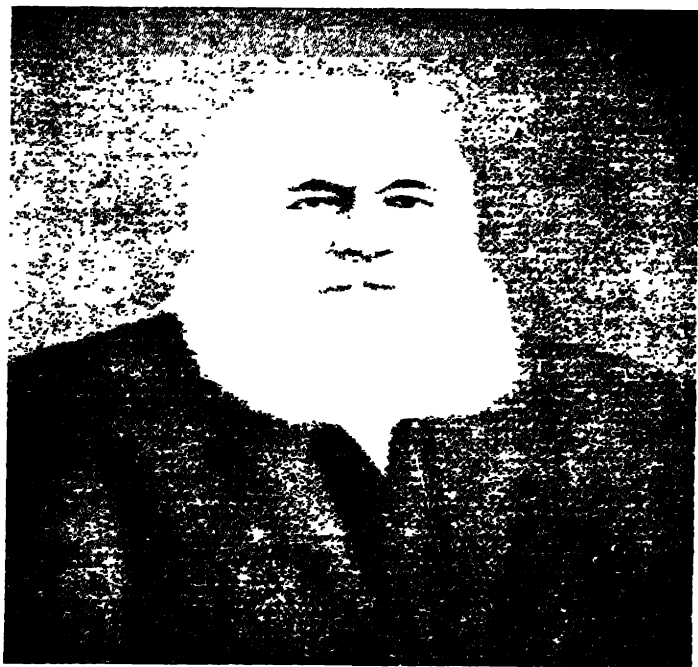
WILLIAM HENRY PERK
(1838 – 1907)

SIR WILLIAM HENRY PERKIN

1838—1907

Perkin was born in London on the 12th March, 1838. He was the youngest son of George Fowler Perkin, the architect and contractor, who died at the age of 63 in 1865. The young Perkin received his preliminary education in a private school. When he was 12 or 13 years of age, a young friend of his showed him some chemical experiments, which produced a profound impression on young Perkin's mind. He at once decided to become a chemist. For sometime he studied chemistry with Hofmann in the Royal College of London, and soon became his assistant. While engaged in this capacity he used to work in spare hours enthusiastically in his private laboratory, which he had fitted up in his father's house. During the Easter Holidays in 1856, when he was only 18 years of age, Perkin was trying to prepare quinine artificially by heating allyltoluidine with chromic acid mixture. Instead of getting quinine, however, he obtained a red powder. By repeating the experiment with crude aniline in place of allyltoluidine he got a black powder, which ultimately proved to be the first synthetic dye.

On August 26th, 1856, Perkin patented the process for making the first coal-tar dye, which he named "Mauve." Soon afterwards he erected a small factory at Greenford Green near London for the manufacture of the dyestuff discovered by him.

Perkin made Graebe and Liebermann's synthesis of Alizarine a commercial success. In 1878, he established his well-known "Perkin's Reaction" and succeeded in the synthesis of coumarin.

Perkin retired from business in 1874 and the rest of his life he devoted to original research. In 1866 he was made a Fellow of the Royal Society and in 1906 he received the knighthood. Besides receiving honorary degrees from the Universities of Oxford, Heidelberg, John Hopkins and Columbia he was awarded the Hofmann Medal by the German Chemical Society and the Lavoisier Medal by the French Chemical Society in recognition of his pioneering contributions to the knowledge of synthetic dyestuffs.

Perkin died at Harrow on July 14, 1907.

take up the career of a chemist.   A further happy chance led him to London into its City School, the only institution of its kind in the country, in which chemistry and natural science were taught.   There he was permitted soon to assist his teacher Thomas Hall, a former student of Hofmann, in his lecture experiments.

At 15 years of age Perkin entered the Royal College of Chemistry as a student.   Since 1845 a second "Giessen" Laboratory was erected in Oxford Street, London.   Hofmann investigated and taught in the spirit and with the fascinating method of teaching of his teacher Liebig.   From all quarters, from home and abroad enthusiastic students flocked around him.

The first task which Hofmann asked of his young student after completion of his analytical course, was one—unpublished investigation on anthracene.   Two years after Perkin's admission, Hofmann made him his private assistant.   And now the world of ideas, the example, the working method, the enthusiasm of the teacher passed over to the pupil.   Perkin lived and worked in Hofmann's spiritual atmosphere, the ammonium bases, above all, aniline, the idol of Hofmann's youth, became his intimate friend (*Hofmann, Chem. News* 3, 354); he investigated the reaction products of naphthylamine (*Proc. Roy, Soc.* 8, 10, 48) with cyanogen chloride and nitrous acid, with ' nitrosophenyline ' and ' nitrosonaphthyline ' or aminoazonaphthalene he for the first time entered the domain of dyestuffs and in his imagination appeared the synthesis of quinine.

And while in day time he helped his teacher—it was the busy time with the phosphorus bases—in the evenings and at every leisure hour his insatiable impulse of investigation, that mysterious bent, which lead to the discoverer unwillingly to his goal, drove him to lonely work in a laboratory scantily fitted in his dwelling place.   There he searched for quinine, which was thought to be derived from allyltoluidine by oxidation.   The comparison of the empirical formula showed this.   But it was not clear how oxidizing agent would act on such bases.   Therefore a preliminary experiment was quickly started with aniline!   This experiment was made during Easter Holidays in 1856.   With

the addition of potassium chromate to an aqueous solution of aniline sulphate, a black, amorphous precipitate was formed.

Such 'colour reactions' had been observed by Runge and indeed by every one whoever has brought aniline in contact with oxidising agents. The literature was not poor on clear proofs of the colour producing nature of aniline. But they lay scattered, forgotten and unattended to, on the path of scientific progress waiting for the hour when a fortunate investigator should un-riddle their mystery. For, " the investigator must follow the path of the path finder," he must esteem every footmark, every broken twig, every fallen leaf (*Kekule's Benzene Celebration, Ber.* 23.1309).

Perkin was this investigator. He investigated the black pre-cipitate—treated it methodically with different solvents, at last he obtained a beautifully violet alcoholic solution. So long this was, however, a scientific discovery only.

The theoretical invsteigator, striving definitely towards his goal was to turn even at this point. That is not the way to the colourless bases as quinine—colours are the sirens on the investi-gator's path. How often Hofmann himself had bade defiance to their enticements, when " in his experiments most wonderful colour reactions shone suddenly forth, from all sides." (*Hofmann, Reply to the festival Greeting of the German Dyestuff Manufacturers, 7th June, 1890*). Armed only with the decolourising charcoal one ventured the colouring phenomena.

Not so Perkin. In him the spirit of the practical discoverer lived at the same time. He tested his coloured solution, whether it could dye and usefully dye.

This was a great stride in those days, when nature still had the exclusive right of the production of dyes. However, as with so many discoveries, the new progress lay almost in the air.

Picric acid was already in use; Murexide was manufactured on large scale chiefly by Robert Rumney in Manchester—daily production amounting up to 2 cwts (*Rep. Br. Assocn.* 1861). Since 1864 it has disappeared from the market. The first experi-ment was made by Albert Schlumberger in 1853 (*Bull. Soc. Ind. Mulh.*, 123, 242) which soon afterwards began a glittering but

short-lasting career under the name of ' Roman Purple' and had likewise found a manufacturing process from uric acid of guano— a technical simplification of the Liebig-Wöhler's method—and its fixing on the fibre by lead or mercury mordants. The same year after long investigations in Lyon Marnas succeeded in transforming the unstable violet of Archil into a light and acid fast dye the "Pourpre francais." This dye fixed itself directly on wool and silk, the cotton had to be "animalised" with albumin or Turkey red. Thus, in 1856, the dyeing technique, the market and the fashion were prepared for the appearance of new artificial dyestuffs. And strange coincidence!—the silk cord which Perkin drew out from the first bath of his aniline dye, gleamed in purple colour. But the dyeing required no mercury mordant and is fully air, light and acid fast. Almost at the same time as with the Roman and French purple its victorious rival appeared.

Now the question stood up—what would a dyer think of it? A sample of the new substance was sent to Puller in Perth and it was favourably judged. At once the idea to establish a new industry took shape. The patent of the dyestuff process was forwarded to the English Patent Office on the 26th August, 1856—the idea to patent in foreign countries was still a remote one. (*The first French Patent taken on the 8th April, 1858 remained ineffective owing to the earlier publication of the English Patent ; a process which occurred frequently in the case of discovery of important dye-stuffs, but which has become impossible to-day*).

The summer vacation was over but Perkin did not return to Hofmann's Laboratory and more; his whole energy was concentrated now to give an industrial shape to his discovery. In the beginning of 1857 he began with limited means, supported by his father and brother, the construction of the first coal-tar colour factory in Greenford Green near London, and in December already the first dye of the firm Perkin & Sons was sent to silk dyers in London. Soon the anxious apprehension of failure disappeared, and the still more depressing anxiety, that the practice would bar his scientific zeal of investigation for ever, passed away. The young factory had brilliant success and in the midst of the towering work Perkin—as is well known—

6

remained true to his science. So, he himself undertook the analytical investigation of his new dyestuff Mauveine [*Perkin, Proc. Roy. Soc.* (1863) XIII, 170; *Journ. Chem. Soc.* 55, 717], investigated the nature of Safranine, which came into being by its side through further oxidation (*Perkin, J. Chem. Soc.* 35, 731), observed the formation of the stable violet out of the unstable Runge's Blue (*Perkin, J. Chem. Soc.* 32, 25), the calcium chloride reaction of the Kyanol, our oldest but still insufficiently investigated Indamine, completed the knowledge of the aminoazonaphthalene and its split-up products (*Perkin & Church, Ann. d. Chem.* (1863) 129, 104; *Perkin, do* 137, 359), and worked later on in the field of artificial Alizarine. But Perkin did not confine his scientific interest to coloured substances only. His investigations on the constitution of aliphatic oxy-acids important also for the industry, were followed by the synthesis of coumarin and cinnamic acid [*Perkin, J. Chem. Soc.* 21, 53; *Ann. d. Chem.* 147, 229 (1868); *Chem. News* 32, 258 (1875], continued by the study of its processes of formation and by their numerous analogues and derivatives. And as after years he once again returned to the rural calm of his laboratory from the noisy atmosphere of the factory and business life, he devoted his whole energy to the solution of scientific problems on the border line of chemistry and physics.

The life of this great discoverer shows a rare combination of an idealistic and practical trend of mind built on the deep foundation of his moral seriousness.

"We have long been detained by the history of the first origin of our industry"—here the reporter interrupted "not only because it furnished at the same time an insight into the nature of the chemical investigation and in the investigator's process of thinking as well as in the necessary coincidence of a present technical requirement together with favourable circumstances of time and place, but also because in the person of the first manufacturer of the coal-tar colours, in his contribution and mind, his education, his combination of theoretical knowledge, practical capacity and energetic will were embodied the traits of our industry. There was no lack of outstanding successors of Perkin in one or the other direction and what one individual
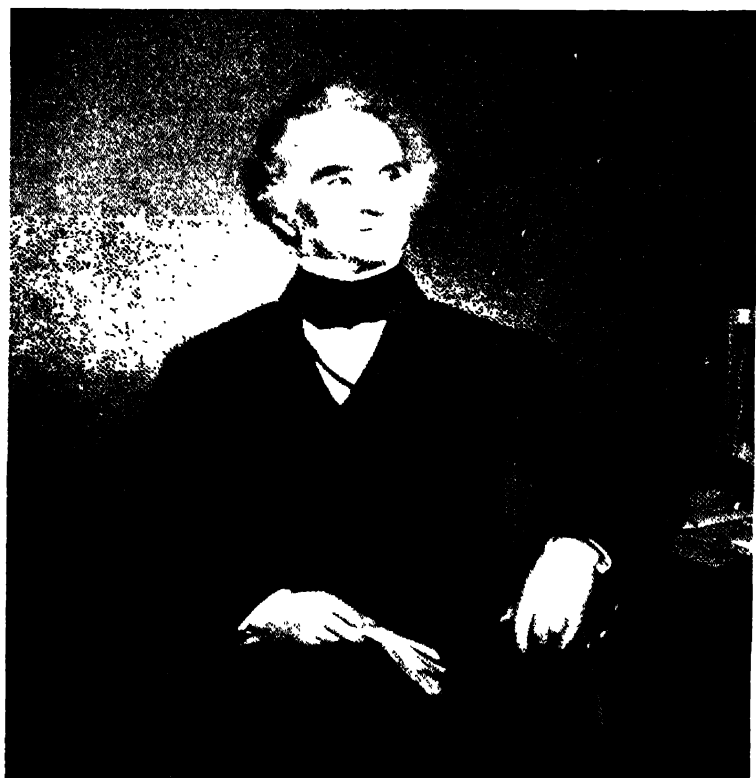
JUSTUS VON LIEBIG (1803–1873)

JUSTUS VON LIEBIG

1803—1874

Liebig was born on the 12th May, 1803 in Darmstadt as the second son of an industrious merchant who traced his descent from an old vigorous stock of Hessian farmers. In the house where Liebig was born, his father, Johann George Liebig, carried on a business for which he prepared by his own hands varnish, lacquer and dyes in a small laboratory. While a little boy, Liebig with an inordinate love for reading went through all the numerous prescriptions that came to the house. With the help of those recipes he experimented to his heart's content with the drugs and chemicals of his father and often visited the neighbouring workshops. A brilliant piece of his work of this period was the preparation of fulminating silver. In October 1820 he began to study chemistry at the University of Bonn. Besides his whole-hearted devotion to chemistry, here he showed extra-ordinary aptitude for Mathematics, Latin, Greek, French, English and later Italian. He also studied chemistry at the University of Erlangen and then proceeded to Paris and had the good luck to become the pupil of the famous French Chemist Gay-Lussac. In 1824 Liebig returned to Germany and at the young age of 21 was appointed Professor of Chemistry in the University of Giessen. The post of the Professor of chemistry in the University of Munich was offered him in 1852, which he adorned until his death in 1873.

Liebig invented the method of Quantitative Organic Analysis now in vogue. In collaboration with his life-long friend Wöhler, he discovered the group of the benzoic compounds and put foroward the radical theory. Liebig also organised systematic courses of chemical instruction. This had a salubrious effect on the growth of the German dyestuff industry in which Germany attained a remarkable pre-eminence. For, well trained chemists devoted their energies and chemical knowledge to the promotion of coal-tar colour industry of the country. Liebig investigated cyanates, cyanides, ferrocyanides, thiocyanates and discovered hippuric acid, chloral, chloroform, aldehyde, benzil, and elucidated the constitution of organic acids and amides. In collaboration with Wöhler he investigated uric acid and its derivatives. He practically laid the foundation of modern agricul-tural chemistry and also worked on physiological chemistry, especially on the elaboration of fat, on the nature of blood and bile and on the juice of flesh. He was a most prolific writer ; as many as 317 contributions from his own pen are included in the Royal Society's catalogue of scientific papers.

Liebig's Annalen, founded in 1832 is still one of the most important journals. For a number of years he edited Geiger's Magazine for Pharmacy. Liebig's laboratory at Giessen was a veritable hive of industry. "We worked from break of day till nightfall," said Liebig, " Dissipation and amusements were not to be had at Giessen. The only complaint which

was continually repeated was that of the attendant, Aubel, who could not get the workers out of the laboratory in the evening when he wanted to clean it." Among those who worked at Giessen under Liebig were: Hofmann, Strecker, Warrentrapp, Kekulé and many others, who in after years themselves became famous chemists.

Liebig not only enriched the intellectual treasures of mankind by his own discoveries but also by the inspiration of his personality and teaching formed a band of disciples worthy to carry on and extend the tradition which he created.

did not possess, was supplemented by other co-workers. But all grades of talents must meet to ensure an all-round industrial success. That is to-day possible only by the harmonious co-operation of diverse talents.

In the process of development of our industry, however, on its erroneous way from quinine to dyestuff and from dyestuff to healing agents and to its further wonderful fructification of science and practice, the truth of Liebig's words presented themselves in bold relief to us [*Liebig, Chem. Letters (3rd Edition) XII letter, page 185*]:

"The theories lead to practical work and investigations. When one works, one makes discoveries,—one digs on brown coal and discovers salt mines, one digs up iron and finds much more valuable ores."

It was also Liebig who once uttered the prophetic words: (*Liebig*, l.c. II letter, page 55). "We believe that to-morrow or the day after somebody will discover a process to prepare from coal-tar the magnificent colour of the madder or the beneficent quinine or morphine."

In Perkin, the student of Hofmann, these words of the great teacher have become the first creative act. In order to reach the artificial production of vegetable dyestuffs and alkaloids, the dyestuff world of the coal-tar had to be opened up first.

The reporter continued—"If I were to describe the difficulties which Perkin had to fight for the technical development of his discovery, for the erection of the factory, the procuring of running capital, the construction of the apparatus—particularly for the manufacture of aniline which was then a laboratory preparation, and for the extraction of dyestuffs with boiling benzene and then with alcohol—finally in his research for practical dyeing and printing methods for the dyestuff furnished with previously unknown basic properties and in its introduction into the market—all those to-day, under the present surroundings, would appear scarcely comprehensible to you. Nothing was there. The fundamentals of a new dyestuff and dyeing technique had to be created. The demand for benzene which could be transformed into aniline which up to that time had found applica-

tion, principaily as crude coal-tar naphtha partly for the preparation of caoutchouc solution for the preparation of water-proof substances—the elderly people still remember the fearful smelling black and white checked 'Macintosh'—partly for burning in the open at the English evening bazars and fairs in lamps of Read Holiday, benzene which in a more pure form was prepared only for certain solvent purposes—who has not heard of Bronner's scouring water—or on a very limited scale was prepared for the preparation of the oil of mirbane (nitrobenzene). Only this demand of benzene set first the tar distillates in motion. For, the costly dyestuff which initially came in the market at the price of platinum special applications had to be found chiefly in the silk dyeing and calico printing. The deep violet dye was 12 times the price of that of Cochineal Scarlet for the wool dyer. In short everything was new: in every direction science, industry and commerce had to widen their mind's horizon.

As this range of vision was broadened, a new world opened, full of fabulous charms—for one a gold field, for the other a prospective field of investigation. Every one turned towards it, driven by an irrestible force, the industrialist, the scientist, the tradesman and the adventurer. The beauty, the fastness, the decisive success of the first aniline dye had a sparking effect. At first the Archil manufacturers recognised its great significance. Rudolph v. Knosp introduced it on the Continent, in France and in Switzerland factories were built (*Through a contract of the 1st January 1859 R. Knosp in Stuttgart won the monopoly of sale of Tyrian purple in Germany, Prussia, Austria, Switzerland, France, Belgium and Holland for 7 years*). One searched for other processes for the violet, observed an abundance of new colour reactions, tested the formation of the dyestuff on the fibre, grasped at the aniline and quinoline of coal-tar, at the naphthalene and phenol, scrutinized all the old and new hints for the coloured transformations of aniline. Soon a new and still more glittering dyestuff was found—the Aniline Red. But nevertheless this was no new scientific discovery.

As early as 1856 the formation of a brilliant red by-product was observed by Natanson (*Natanson, Ann. Chem. Pharm. 98*

297) by heating aniline with ethylene chloride and two years later by Hofmann (*Hofmann, Proc. Roy. Soc. 9, 284, 17th June* 1858). As with all patent processes one has tried to give subsequently the character of an industrial aspect also to this scientific discovery, in the fight against the French monopoly of Fuchsine, during the preparation of his carbotriphenyltriamine from aniline and carbontetrachloride. Only Hofmann described in detail the striking colour character of, the richly coloured mother liquor of the colourless product investigated by him. But the discoverer did not go beyond the scientific discovery. The utilization was not tried. Even what once Runge had done with his Rosolic Acid the testing of the colour properties lay far from his scientific aim.

There Emanuel Verguin, a professor at the College de Lyon, made the pioneering technical discovery. With lucky instinct he seized the anhydrous metal chlorides, first the old spirit Libavii, heated it with the technical aniline containing toluidine and easily and quickly the first 'dyemelt' originated. But he did not himself exploit his discovery as Perkin, it was handed over to the silk dyer Renard Brothers in Lyon. On the 8th of April 1859 they took the first French Fuchsine patent, four days after the first English one. They indicated the anhydrous chlorides of tin, mercury, iron and copper as the reagents for the production of the red dye of the colour of the fuchsine flower. The French Brevet brief claimed, however, not only these processes but also the use of this new dyestuff to dye or print all textile fibres—silk, wool, cotton and yarn and moreover hides and feathers. In a later supplement the claim was raised up to the dyestuff itself, detached from the method of its preparation. They gave it the formula $C_{24}H_{10}N_2O_3$, which was later proved as erroneous by Hofmann.

This success of Fuchsine was momentous—much greater than that of Perkin's violet. Such a dyestuff had never been seen before. How dull appeared the rose-colour of Cochineal in comparison. Its seductive brilliance forced back all doubts against its defective fastness, even if the industry was thrown on the dangerous path of non-fast dyes by it. The fashion wanted it. The fair sex loved also the transitoriness provided

it was new and becoming. Therewith the immediate mass pro·
duction ensued. One had only to melt and to despatch the
pasty melt in stone containers; in the subsequent use of mercury
salts, to pour out the separated mercury beforehand. The
melt was much costlier than this noble metal and the dyer him-
self boiled it before use. However, the manufacturer soon takes
over the easier work. One erects boiling tanks, filters and
precipitation vats. It is known that it originated from a photo-
grapher's lucky idea, to advise a dyer struggling in vain against
the light-instability of Lauth's "Aldehyde Blue." From the
preparation of Indigo Carmine the art of precipitating with
common salt became known. So the "salting out" of the dye-
stuff was first introduced in the coal-tar dye technique in the
case of Fuchsine. Then it was dried, powdered and alcoholic
or acetic acid solutions were prepared. A separation of fuchsine
from its yellow and violet soluble admixtures took place in a
later period only and for a long time one spoke of yellow and
blue tinted Fuchsine, as essentially different dyes under a series
of fanciful names. Every body now turned to the easy and
profitable melting process. The era of mass discoveries began.
Everything was investigated, every thing that gave red colour
was patented—every metallic salt: chloride, bromide, iodide,
fluoride, sulphate, nitrate, chlorate, bromate, iodate; one melted
with iodine and iodoform, heated with nitric acid and did not
even hesitate to experiment with titanium, uranium and silver
salts. In the patents one included of course the homologues
and analogues of aniline. Everybody was a discoverer. Every
one dreamt of honour and treasure. The gold fever started and
was soon followed by its dark attendant—the ruthless conflicts.

After a short time the better conquered the good. Stannous
chloride was replaced by mercuric nitrate, with which the
industry struck its first powerful roots in Germany also. (*R.
Knosp, Engl. Pat.* 1859). Mercuric nitrate was finally replaced
by concentrated solution of arsenic acid.

In England Henry Medlock took the first patent of arsenic
acid-Fuchsine on the 18th of January, 1860. But, embarrassed
by the prejudice of the time, which required anhydrous agents
Medlock patented the inactive anhydride, the dry arsenic acid,

and following the general custom he patented too much: The formation of dyestuff hot or cold. In the first patent-conflict which broke out pretty soon, the dry acid still admitted a liberal interpretation of the solid hydrate of arsenic acid, current in the market; soon however, a new opponent, Read Holliday discovered the weak point. The little word 'or' the alternative between a realisable and a non-realisable process made the patent fall through. A supplementary improved process was opposed now by other English manufacturers also. The fuchsine monopoly died away for ever after an unheard of brilliant domination of over five years. But the prize was won not by the English but by the patiently waiting German industry. For its much cheaper product the extensive English market was opened now.

Previously already the French monopoly which had remained unshaken had led after a passionate dispute to the immigration to Switzerland of the defeated patent owner [*Gerber-Keller (French brief of 27th October,* 1859) *established his factory in Basel in* 1864] of the mercuric nitrate process and thereby advancing the Swiss industry. And while among the free competition the price of the dyestuff sank in leaps and bounds, improvement after improvement were introduced in factories, the secure monopoly in its natural course led further on to the unsound drawing by banks, on the basis of already attained and never dwindling gains. The firm of Renard Freres & Frank was converted into a joint stock company with a capital of four millions. The best co-workers withdrew. The discoverers were satisfied with shares. That was the beginning of the end of the mighty company, La Fuchsine (*In the factory at Roche-cardon at the beginning. of* 1864, *crystalline fuchsine was prepared with a yield of only* 15.5% *at the material cost of* 47.78 *frcs. per kilo*). France was permanently hurt. These monopolies have, as we have seen, badly affected the development of the coal-tar colour industry. They contain a serious lesson! One shall not misuse the protection of discovery. The set back will never fail to appear. This is shown later in other cases also.

However, let us turn again to Medlock's patent. It came into the possession of the firm: Simpson Maule and Nicholson,

a factory of pure chemicals in London, the model of our 'Kahlbaum'. It had already undertaken first for Perkin's requirements the manufacture of aniline, which at the end of the year 1860, was brought in the market at a price of 24 marks per kilo. Nicholson immediately discovered the right agent for the formation of aniline and the heating of a mixture of aniline, toluidine and cumidine or their mixture with a strong solution of arsenic·acid was patented on the 25th January, 1860. But when he learnt that Medlock had preceded him by seven days with the arsenic acid he dismissed his own good patent and acquired the bad one.

Also human error and accidents had to contribute to the free development of our industry.

The unprecedented success of the new fuchsine process, kindled the fire to still brighter flame. Everybody would participate, no body would be debarred, every one tried to save what could be saved. Everything one had in hand, was boiled with aniline now available—finally, the dyestuff itself! The appearance of violet by-products in the fuchsine melt pointed to secondary actions of the aniline. Charles Girard and Georges de Laire, students of Pelouze, found in the laboratory of their teacher, in the mint of Paris, independent of Nicholson and shortly after him, the arsenic acid process and in the further course of their investigations the epoch-making phenylation of Fuchsine (*de Laire and Girard Engl. Patent* 1860, *May* 26, *No.* 1300).

[*Charles Girard, born in 1837 in Paris, from 1854 assistant to Pelouze, then after a short practical career in Brentford near London, chemist of La Fuchsine near Lyon, worked there for 18 months 1868-1870 on Methyl Violet and Iodine Green with Hofmann, and then directed the firm of La Phenyline near Ris-Oranges (diphenylamine etc.), published in 1873 with de Laire, the first comprehensive work on dye-stuffs (Traite des Derive's de la Houlle etc.) and worked with Berthelot and Wurtz. Since 1878 director of the City Laboratory in Paris (friendly private communication from E. Noelting.)*]

[*George de Laire, born in 1836, entered on completion of his University studies in 1856 the laboratory of Pelouze and*

turned since 1859 to the joint works with Girard, in which he independently discovered the special action of aniline on rosaniline acetate and in 1873-74 the blue and green dyestuffs from alkylated diphenylamine. Since 1875 occupied with investigations on artificial perfumes, de Laire became successful owner of the French Tiemann-Haarmann vanillin patents and joint owner of the Baur's artificial musk patents (friendly private communications of E. Noelting.)]   •

Their English Aniline Blue patent dates from the 12th February 1861. They entered as chemists the Renard Freres & Frank in Lyon. The French firm went into an all out alliance with the English licence bearers of the patent: Simpson, Maule and Nicholson. A brilliant series of spirit-soluble and acid-fast violet and blue dyes, more fast to light than Fuchsine were the basis of a prosperous manufacture and forced rapidly their way into the silk and wool dyeing concerns. The more costly Perkin's Violet remained confined principally to the calico printing. For the Indigo, by far the more for the patent blue of the yellow and red of potassium ferrocyanide the first competition grew up.

Almost at the same time one's attention was turned to the Rosolic Acid for Kolbe and Schmitt's synthesis of salicylic acid and Jules Persoz' discovery of a method of preparation in which carbolic acid was heated with sulphuric and oxalic acids. Marnas in Lyon converted first only the red dyestuff in alkaline solution by heating with ammonia under pressure into the acid-fast Paeonine Red, finally he also boiled Paeonine with aniline and obtained the brilliant blue Azuline. However, the secret was guarded. The mysterious dyestuff yet appeared in the market as the first light-fast blue—the more beautiful but completely light-unfast Cyanine from the cinchonine of Greville Williams (*English Patent No.* 1090, 1859; *Hofmann, Proc. Roy. Soc.* 12, 410) had already preceded it in the market—before the Aniline Blue in 1861. On the 28th July 1862, the English patents of Guinon, Marnas and Bonnet were published and the origin of the red and blue conversion products of Rosolic Acid was unveiled. [*English Patent (W. Spence)* 1862, *No.* 2130, 2132. *The Azuline appeared in 1861 at an exhibition in*

Manchester, arranged for the meeting of the British Association.
It was perfumed with naphthalene.]

However, many years passed before one realised that the practice here had unconsciously found, although incompletely, a synthetic method of preparation of Aniline Red and Aniline Blue. The Rosolic Acid itself, the yellow coralline or Aurine, remained unprotected and developed into a new branch of industry, specially after introducing it successfully in the form of the fiery Turkey red lake as pigment also in the wall paper prints. This new application of carbolic acid got a still greater significance however, through the technical requirement, which at once called forth a purer raw material than hitherto available. Thereby Crace Calvert in Manchester jointly with Charles Lowe, was led to establish a concern for the preparation of carbolic acid, which, coming out from the workshop in ever purer form became not only serviceable for the dyestuff industry in immediate consequence first for Corallin and Picric Acid, but also for the blissful application in the antiseptic (*Calvert, Chem. News* 16, 297). And finally experiments on the method of formation of the Corallin, in connection with Hofmann's explanation of the Aniline Red formation, led to the preparation of completely cresol-free phenol from phenolhydrate for therapeutic use (*Ch. Lowe, letter communication* 1867).

But let us again turn to the fuchsine.

The arsenic acid-melt compelled the industrialist to remove the poisonous substance from the dyestuff as far as possible. One began to purify in a rational way, to separate from one another the soluble and insoluble dye-mixture of the raw melt and thereby to obtain the crystalline Fuchsine. Nicholson employed excess of milk of lime, let it boil, and from the colourless filtrate crystallized his calcium base—Hofmann's Rosaniline. At the same time he isolated the first yellow basic aniline dyestuff, Hofmann's Chrysaniline.

Thus the London World-Exhibition of 1862 drew near, when for the first time chemistry was to unveil its new splendour of colours to the great masses. The impression was deep, not less than the one which lately physics called forth at its first electrical exhibition. One looked into a new world. In the

glass cupboard of Perkin & Sons one could pursue the development of the industry from coal-tar to the crystallized Aniline Violet and its numerous useful applications.   In the centre was a block of the pure dyestuff with metallic lustre, the final product of the purified chemical out of 2,000 tons of coal-tar, but sufficient to print over 100 English miles of calico.   One saw the metamorphising influence of the new industry in all branches of dyeing. Then followed the cupboard of Renard Freres & Frank containing stupendous quantities of Fuchsine, 'the Violet Imperial,' and the ' Bleu de Lyon.' Guinon, Marnas and Bonnet showed their Azuline, besides Picric Acid and the 'Pourpre francais'; Roberts Dale & Co. their new process to prepare Mauve with copper chloride, Lloyd and John Dale (Engl. Pat. 1861, No. 701) the fixing of the violet on cotton fibre with tartar emetic and tannin; Crace, Calvert, Lowe and Clift (Engl. Pat. 1860. No. 1426) the first production of Emeraldine and Azurine, the forerunners of Aniline Black in the fibre.   Murexide was also not missing.   The glance at a stately series of exhibits of benzene, nitrobenzene, phenol, aniline, naphthylamine and their coloured derivatives convinces us what an expansion the tar product industry has already attained in England and on the continent. Germany was represented by Knosp, Oehler, Jäger, Peters and Brönner.

The crown of the exhibition is however, hidden in the glass cupboard of Simpson, Maule and Nicholson. There on the velvet cushion the incomparable 'Magenta Crown' is built up (.1 crown almost a metre in height was obtained from a solution of rosaniline acetate worth £8,000 sterling—Hofmann, Chemical News 6, 94), out of centimetre long, completely formed, smooth surfaced crystals of the pure rosaniline acetate. Next come the wonderful colourless base and its magnificently crystallized chlorhydrate, sulphate, arseniate, oxalate and picrate.

Further the still mysterious Regina Violet of Nicholson— a monophenylated rosaniline—and its new yellow dyestuff, the pure Chrysaniline nitrate and finally the raw materials and intermediates of the manufacture are exhibited.

With this, material brought to light by scientifically illuminated technique to which Nicholson soon added the colour-

less base and the crystallized salts of the Aniline Blue, Hofmann could start the series of his brilliant investigations on aniline dyes and create for the later investigation of their constitution the first sound foundations.

[*Edward Chambers Nicholson, born in January* 1827 *at Lincoln, entered in October* 1845 *after finishing his training in a pharmaceutical and chemical laboratory the newly established Royal College of Chemistry, with Sir Frederic Abel, one of the oldest students of Hofmann. In* 1850 *Nicholson left his position as an assitant there, in order to devote himself to the foundry department at the works of Fothergill, but an illness forced him to give up his profession so successfully begun, and in* 1853 *he established with Simpson & Maule in Lockfields, Walworth, a factory of pure chemicals and laboratory preparations out of which then, after his obtaining the Medlock's fuchsine patent (for* £2000 *sterling) the dye factory in Hackney Wick developed. In August* 1868 *Nicholson retired and died on the* 23rd *October,* 1890. *He was a man of untiring energy, which also stamped his external appearance. (Friendly communication of Mr. Arthur G. Green, Cf. also J. Soc. Chem. Ind.* 1890, 1023.)]*

Already before the opening of the World Exhibition his first work on Aniline Red was published. (*Hofmann, Roy. Soc.* 12, 2; 6th *March* 1862). It threw light on the confused mass of fuchsine literature, showed that the red dyes emerged from different processes of formation and denoted under different names must be in pure condition the salt of the same colourless, hydrated base which in expectation of possible homologues and analogues received the name Rosaniline, reminding colour and origin of the Fuchsine. Neutral, acid, red and yellow salts were described.

By the application of the same method with which Hofmann once for the first time converted nitrobenzene, obtained from coal-tar, into aniline by the action of nascent hydrogen from hydrochloric acid and zinc, but better still with ammonium sulphide, he now reduced Rosaniline to the colourless salt forming anhydrous leucoaniline. During the transformation into the colourless condition the dyestuff "like the Indigo Blue" absorbs two atoms of hydrogen. However, not briskly, but slowly and

extremely incompletely, the colour returns with the admission of air. In addition the leuco-aniline requires a careful treatment with oxidising agents. And then diazo-compounds of both Rosaniline and leucoaniline, furnish fulminating platinum salts.

In this work we recognize the leading idea of the later investigations of dyestuffs.

The following year brought Hofmann's successful elucidations. On the necessity of the presence of toluidine in the "aniline for red" the comparison of the rosaniline formula with that of toluidine and aniline allowed immediately the setting up of an empirical equation of formation. But Hofmann (*Hofmann, Proc. Roy. Soc.* 13, 1864, 490) established this equation only in the following year in order to rectify the erroneous views on the process of formation of the Aniline Red (*Hugo Schiff, Ann. Chem. Pharm.* 127, 1863, 337). At the same time, he tried for the first time to express by typical formulae the constitution of Rosaniline, Aniline Blue and Iodine Violet in which the nitrogen mediates in the coherence of the carbon atoms. Previously he had already (*Hofmann, Proc. Roy. Soc.* 13, 1863, 6, 9) published the investigation of Chrysaniline simultaneously with that of Aniline Blue. Through the theoretical knowledge of the blue dyestuffs as triphenylated rosaniline he had been led directly to the great commercial discovery of the triethylated Fuchsine and the analogous "Iodine or Hofmann's Violets."

So in short time a flood of light was thrown on the aspiring industry. Science has broken through the mist of planless experiment and speculation!

Already the last and most remarkable achievement of the pure empiricists was the discovery of Aniline Green [*Cherpin, 1863, Engl. Pat. Usebe 1863, No.* 254 *Eugen Lucius (Hydrogen Sulphide and sulphurous acid) Engl. Pat.* 1864 *No.* 200. *V. Miller and Plöchl, Ber.* 24, 1700.] It is known, that it originated from a photographer's lucky idea to advise a dyer struggling in vain against the light-instability of Lauth's "Aldehyde Blue" (*Lauth, Soc. Chem. Paris, Rep. Chem. Appl.* 1861, 273) to fix the dye like the photograph with the '*fixateur par excellence*," the sodium thiosulphate. This good advice not only gave the immediate impulse to a flourishing manufacture

of the first artificial green dyestuff, but made its after-effects felt still many years afterwards, upto "Lauth's reaction" and to the synthesis of our present day Methylene Blue.   One had come to know the first sulphur containing dyestuff, had explained its formation by the action of hydrogen sulphide (*Hofmann, Ber.* 3, 761) or "nascent sulphur" and arrived finally though perhaps unconsciously or by a similar association of ideas, to the "sulphuring" and "fixing" of unstable Indamines by hyposulphite.

With Hofmann's communications causing the most lively interest the scientific investigation had penetrated into the work-shops of the industry even from the year 1864. After such obvious successes the sure way to further progress seemed to ask to get to the bottom of the nature of dyestuffs, their pro-cesses of formation and starting materials.

One year more, and there came the illuminating day of Kekulé's theory. The time of painful stress and search of the industry had gone; it entered into the wider fields of its develop-ment keeping pace with the well planned completion of the aromatic field.

Here the reporter concluded—" Now I shall try to describe the most important representatives of our dyestuff families and the further processes of their development."

"Almost the whole of the decade belonged mainly to the aniline dye technique and principally to the working in the field of Rosaniline. At its beginning stood the induline group (*Engl. Pat.* 1863, *No.* 3307, *Dale & Caro*) and Safranine; the only representatives of the naphthalene dyes were "Manchester Yellow" (*dinitronaphthol, "Martin's Yellow," Engl. Pat.* 1864, *No.* 2785, *Dale Caro and Martius; Martius, Ber.* 1867, 519 *and "Magdala Red" Engl. Pat.* 1868, *No.* 225, 2290, *Clavel*), of the phenol dyes: Picric Acid and Coralline, of the acridine group: the "Chrysaniline" and "Chrysotoluidine"; of the azo dyes the "Vesuvin"., phenylene—"Bismark" or "Manchester Brown" (*Engl. Pat.* 1863 *No.* 3307, *Dale & Caro; first observed by Martius; H. Caro & P. Griess, Zeitschr. f. Chem.* 1867, 278) ; and of the diphenyl derivatives: the Palatine Orange (*Bad. Anil. Sodaf. H. Caro,* 1869).

In the Calico printing the production of the Aniline Black (*John Lightfoot, Engl. Pat.* 1863, *No.* 151) in the fibre won an ever-rising significance, chiefly when Charles Lauth succeeded in replacing the soluble copper salts of the originally used oxidation mixture of potassium chlorate and copper chloride by copper sulphide which appeared in reaction only after printing, thereby he achieved the first decisive improvement. [*Lauth, Engl. Pat.* 1864 *No.* 1409. *Compare the excellent monograph of Noelting, Hist. Scient. du Noir d'aniline* (1889); *Noelting and Lehne—Aniline Black and its application* (*Berlin, J. Springer* 1892)]. [*Charles Lauth was born in* 1836 *in Strassburg, studied in the University there; after his promotion he became assistant of Gerhardt then, in* 1853 *of Persoz in Paris and in* 1857 *director of the factory of Depouilly Frer's & Co. Since* 1861 *Lauth made his numerous investigations in dye-stuff in a private laboratory; became in* 1867 *scientific adviser to Poirrier and from* 1887 *director of the porcellain manufacture in Sevres. From* 1887 *he occupied himself again with the investigations of dyestuff in his private laboratory.* (*Friendly private communication of V. E. Noelting*)]. Into the yarn and piece dyeing of cotton also this important dye was gradually introduced replacing the acid and light sensitive blue-wood black. Further improvements came from the co-operation of prominent dyers and printers, particularly of the big Mülhäuser colorists.

In the silk and wool dyeing industry, however, Fuchsine and its brilliant phenylated and alkylated derivatives ruled the market and the fashion. Soon the Iodine Green was found in the mother liquors of "Iodine Violet" and with a dyestuff which imparts a lively green tone also to tanned cotton. But while the Iodine Green displaced the Aldehyde Green, Hofmann's Violet was to become a dangerous opponent to the less beautiful phenylated Rosaniline, the fall of Iodine Violet and Iodine Green was yet unnoticeable. At the following World Exhibition in Paris in 1867 the *Violet de Paris* from dimethylaniline appeared. By further alkylation of this Methyl Violet with methyl iodide then with methyl nitrate and finally with chloromethyl the Methyl Green was obtained (*Lauth and Baubigny, Ber.* 6, 825). A devastating explosion in the preparation of methylnitrate occurred

in Bubeland on the 23rd June, 1872, with the sacrince of the gifted scientist Ernst Chapman. Crystallized Methyl Green was prepared by means of methyl chloride first in 1873 by Wischin and in 1874 by Monnet and Reverdin.

Already at the second World Exhibition in Paris in 1878 the victory of the violet and green dyestuff derived from dimethyl aniline was finally decided. To Fuchsine was left principally the vast field of its blue phenyl derivatives, whose technique had been developed to great height much earlier by the application of pure " aniline for blue ", a result of Hofmann's elucidation, as well as by the choice of pure and uniform Rosaniline with the addition of benzoic acid furthering the phenylation. [*The still unexplained action of benzoic acid was first observed in 1862 by Wanklyn in Heidelberg. The addition of sodium acetate to the blue melt as a result of an accidental use of aniline containing acetic acid in the factory of Müller-Pack in Basel in 1862, has been used for a long time.*] By the introduction of Sulphogroups into the Aniline Blue, according to the process of Nicholson (*Engl. Pat.* 1862 *No.* 1857 ; *Ber.* 5, 417), the spirit-soluble dyestuff was converted into the water or alkali soluble dyestuff and thereby a more extensive application of it in the dyeing industry was made possible. The first still insufficiently phenylated *Bleu de Lyon* was followed by the even in artificial light pure blue *Bleu de Lumiere* and Nicholson's "Opal Blue" from pararosaniline. However, these perfect products of the aniline blue processes also were soon rivalled by diphenylamine blue, prepared directly from diphenylamine, by Girard and de Laire (*Engl. Pat.* 1866 *No.* 2686).

So we see, how during the period between the London and Paris World Exhibitions of 1862 and 1878 respectively, the branch of the aniline dyestuffs was developing to ever increasing life under the influence of Hofmann's scientific teaching. The methods which Hofmann found out or as methods recognized, the aniline derivatives which he discovered, the processes of formation which he explained, the analogies which he stated, all of them were absorbed by the technical factories and led under the pressure of progressive demand for better and cheaper

dyes to transforming, improving or simplifying methods of the
oiginal processes.

In this metamorphosis the fuchsine arsenic acid fusion also
took its part. The accumulation of arsenic residues, the scruple
against the dyes prepared with a poisonous substance had
stimulated experiments with nitro-compounds, particularly with
nitrobenzene from an early time. Could one not combine by
the action of an oxygen carrier the reduction of nitrobenzene to
aniline with the oxidation of aniline to a dyestuff? From this
idea emerged Erythrobenzene, exhibited already in London in
1862 (*Laurent and Castelhaz, Engl. Pat.* 1861, *No.* 3225) and
4 years afterwards the nitrobenzene fuchsine process of Coupier
(*Coupier, Ber.* 6, 423; *Brünning,* 25, 1072). A mixture of
" aniline for red " was heated with nitrobenzene, iron and hydro-
chloric acid. The results which Coupier obtained on a large
scale in 1868 were very promising but the German dyestuff
industry only succeeded in the course of the following years in
developing this method into a process for displacing gradually
the arsenic acid fusion.

According to the same method but by the use of pure aniline
Coupier obtained (*Engl. Pat.* 1867, *No.* 3657) simultaneously a
product rich in Induline, his " *Bleu noir* ", from which according
to the process of aniline blue sulphonic acid, he prepared the
first water-soluble Induline and thereby since the beginning of
the year 1870, furthered immensely the introduction of this
class of dyestuffs in the dyeing industry.

Also Safranine which had come into the market from
Switzerland since 1868 had by the time of the Paris Exhibition
developed into a powerful branch of this industry and had found
a firm footing mainly in the dyeing of cotton. Hofmann like-
wise turned his scientific interest to Induline and Safranine
(*Hofmann and Geyger Ber.* 5, 472, 526).

In all these fusion processes of the first aniline dyes,
however, there was not yet the question of a true synthesis of
the dye and the investigations of these dyestuffs bore mainly
descriptive features. Of none was the structure known for
certain. There were plenty of speculations

7

Nevertheless, a new era with new aims had already begun. Adolf Baeyer and his school entered the arena of investigation of the dyestuffs, and the works of Peter Griess had led to the unprecedented practical results.

Let us now go back again to the end of the sixth decade. At the Technical High School in Berlin—the then " Industrial Academy" Adolf Baeyer, the first student of Kekulé was teaching.   He had already published jointly with Knop his pioneering work "Investigations on the Indigo Blue Groups" (*Baeyer & Knop*, 1866, *Ann. d. Chem.* 140, 1).   The elucidation of the nature of Indigo Blue was the pointed aim of these papers, which Baeyer after 17 years brought to a brilliant close, crowned by the synthesis of the "artificial Indigo", when he could communicate that " the place of every atom in the molecule of the dyestuff has been established by experimental ways " (*Baeyer*, *Ber.* 16, 2188 (1883).

With this statement of Baeyer the new orientation of the dyestuff chemistry was characterized.

The main result of those first investigations was the stepwise degradation of isatin to dioxindole and oxindole and when Baeyer shortly afterwards discovered his method of reduction of aromatic compounds with zinc dust, a method of very great consequences, he also succeeded in removing oxygen from oxindole and thereby to prepare indole, the 'mother substance' of the indigo group (*Baeyer*, 1866, *Ann. d. Chem.* 140, 295).

The next fruit of this method of reduction was the discovery of the true mother substance of Alizarine.   In Baeyer's laboratory Carl Graebe had already previously completed his important "Investigations on the Quinone Group" (*Graebe*, 1867, *Ann. d. Chem.* 146, 1).   By starting from chloranil and elucidating the nature of the coloured and colourless derivatives of the tri- and tetrachloroquinone he had reached a new theoretical outlook on the structure of these groups—the basic substances quinone, quinhydrone and hydroquinone.   In these investigations the coloured and colouring chloranilic acid of Erdmann was recognized as dichlorodioxy quinone.

Analogous phenomena were disclosed at once in the domain of naphthalene (*Graebe*, *Ber.* 1868, 36; *Ann. dd. Chem.* 1869,
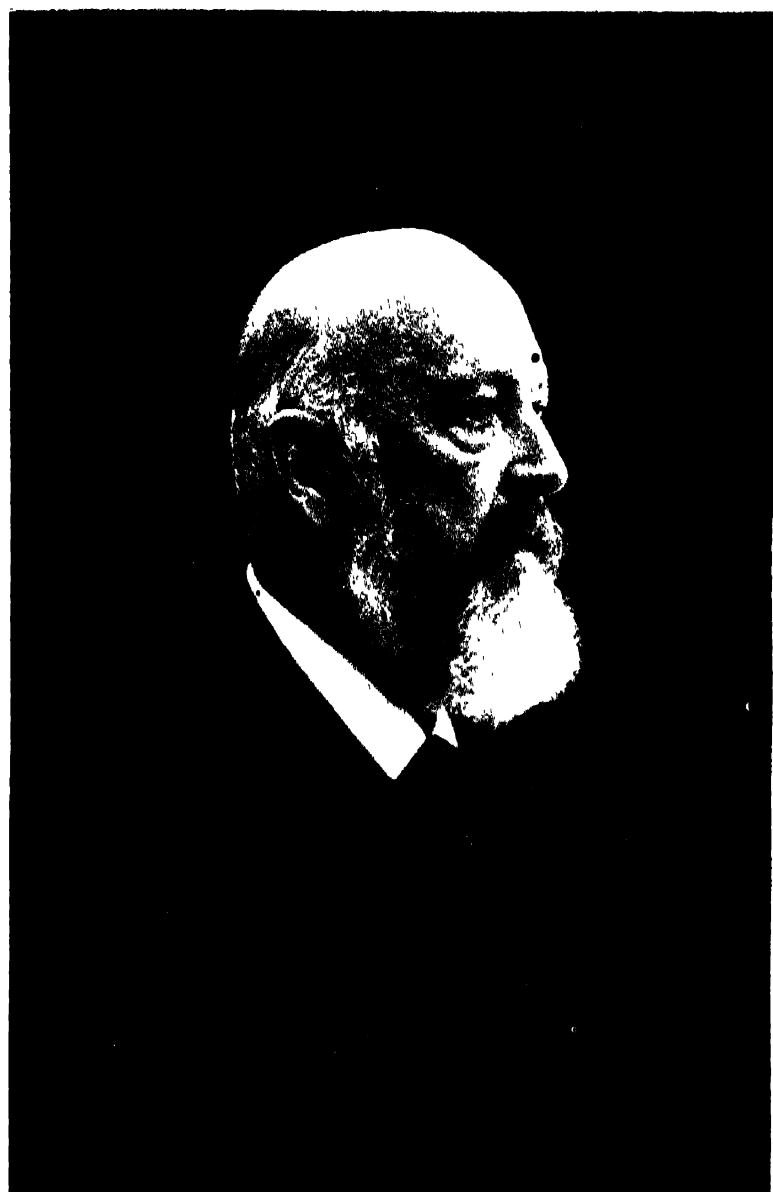
ADOLF VON BAEYER (1835 1917)

JOHANN FRIEDRICH WILHELM ADOLF VON BAEYER

Adolf Baeyer was born in Berlin on the 31st October, 1835. His father Johann Jacob Baeyer, an originator of the European gradimetry worked at that time as the chief of the Prussian General Staff with the astronomer Bessel in the triangular survey in East Prussia. From his very boyhood Baeyer showed a deep and one-sided love for natural phenomenon and a strong bent towards chemical experiments, which he retained to the good old age. His inquisitive nature is manifest from the following anecdote. At the age of 8 he accidentally came across 8 seeds of date palms which he planted in pots and irrigated one with water, the other with milk, the 3rd with wine, the fourth with ink and so forth in order to see the effect of these on the seedlings. At the age of 12 he succeeded in his first chemical discovery of the preparation of the double salt of copper and sodium carbonate. For a time he studied physics and chemistry at the Friedrich Wilhelm Gymnasium at Berlin but soon he left Berlin for Heidelberg to study Chemistry under Bunsen. Here he came in close intellectual contact with Kekulé, Roscoe, Lothar Meyer, Butlerow, Lieben, Beilstein, Pebal and Schischkoff. In 1858 Baeyer obtained his doctorate degree. Baeyer's own teacher was Kekulé, who was then at Heidelberg. In 1871 he was appointed professor of chemistry at Strassburg and five years later he migrated in the same capacity to Munich. He is well-known as the founder of the Strain Theory (1885) and he enjoys the reputation for his synthesis of Indigo, though his method did not prove of commercial success. He also worked on organic arsenic compounds, uric acid group, phthaleins, terpenes, and many other organic substances. He was awarded the Davy Medal in 1881 by the Royal Society of London in recognition of his researches on Indigo and the Nobel Prize for chemistry in 1905.

Baeyer worked for work's sake. He never cared whether his researches had been utilized by others in the development of flourishing industries. He was also very generous in his dealings with his students and assistants. His assistant Graebe working under his direction attained immortal fame by the synthesis of Alizarine and Baeyer was never jealous on this account. Even at the height of his fame he used to work strenuously in his laboratory. Once an unknown chemist, who was jealous of his position said, " Well Professor, you are very lucky in your experiments." Baeyer answered, " I have got no better luck than yourself but the difference lies in the fact that I carry on more experiments than you do."

Baeyer was a man of reserved nature. He never liked to participate in scientific discussions in congresses and public meetings. He was out and out an experimentalist and had a distaste for theorising. Baeyer built a flourishing school of chemistry. Among the host of his students who extended the bounds of organic chemistry in its dyestuff and other branches, mention may be made of Otto and Emil Fischer, R. Willstätter, W. Königs, L. Claisen, Cl. Zimmermann, P. Friedländer, Th. Curtius, H. V. Pechmann, E. Bamberger, W. H. Perkin, jr., E. Buchner, W. Dieckmann, O. Dimroth, H. Wieland, J. Meisenheimer, C. Duisberg, G. V. Brüning, O. Aschan, W. A. Noyes, W. Ipatjew, P. Walden and M. Gomberg.

the simultaneously acquired knowledge of the oxidation product of the anthracene of Laurent and Anderson as anthraquinone, they entered the path to the synthesis of the madder dyestuff according to the methods given by the theory. Fortune favoured the discoverers. None of the numerous theoretically possible coloured but not colouring isomers of the Alizarine but the latter itself resulted within a year out of the potash fusion of the dibromo-anthraquinone obtained by them through different routes. (*Graebe and Liebermann, Ber.* 2, 14, 332; *Ann. d. Chem.* 7, *suppl.* 257; 160, 121). Subsequently one perceived that here for the first time, the apparently theoretically important question of position alone had been of outstanding significance (*Liebermann, Ann. d. Chem.* 183, 147), that the hydroxyls of the Alizarine occupy the neighbouring positions like those of the pyrocatechol (*Baeyer & Caro, Ber.* 7, 974) and that on this alizarine-position depends mordant colouring action. The Alizarine from coal-tar was discovered. In their first communication to the German Chemical Society they rightly pointed out the far-reaching significance which a new branch of industry would attain and which was based on the artificial preparation of Alizarine from a constituent of the coal-tar.

How should the coal-tar colour industry not immediately have recognized this significance? From it was discovered, almost with the speed of wind, the present method of preparation nearly simultaneously in Germany and England in the spring of 1869. And surprising was the industrial result, which was obtained by the alkali fusion of the anthraquinone sulphonic acid. Along with Alizarine, attendants scarcely less valuable were formed and were later known as flavo and anthapurpurine, the assembly of these dyes is the "artificial Alizarine." In partnership with Graebe and Liebermann the English patent on the improved process was taken from the German industry. Prussia refused the protection, in France and America one relied on the strength of the monopolies granted to the first discovery. And what a lucky star shone over the German industry, that its English patent (*Caro, Graebe and Liebermann, Engl. Pat.* 1869, *June* 25, *No.* 1936) preceded the one of its great English rival Perkin only by one day. (*Perkin, Engl. Pat.* 1869, *June* 26 *No.* 1948).

This led to the reciprocally furthering union, and the English market remained opened to the German sale. The patents reached their undisturbed end after 14 years. In France, however, the industry took no lively development, and in America the monopoly fell even before its expiry after years of struggles.

The young industry was immediately started with English energy and German thoroughness. Already in the very same year Alizarine appeared in the market. And now the first annihilating fight of an artificial dyestuff against the products of nature began. The anilines known up to that time had been only substitutes or colouring materials of never dreamt of beauty and originality. Now, the age-old genuine fast dyes themselves emerged from the chemical workshops, followed by not less genuine and valiant kindreds. At once the opponent was attacked at his weak point. A root of only 1-2% dyestuff content, a costly cultivation on valuable European country side, long and complicated methods of dyeing! The dyestuff had to fix along with its discolouring companions, and which caused protracted and costly *Avivagen*, combined with loss of dyestuffs particularly the difficult and tedious manufacture of the Turkey red, with its repeated mordant and dyeing processes, and finally the necessity to prepare from roots poor in dyestuff, through price-raising processes of extraction the alizarine and purpurine in purer and more concentrated form for the steam colour-print. All this was stressed from the very beginning against the natural product and was in favour of the artificial alizarine as it entered the field of competition almost analytically pure and promised in the immediate future the long expected reform of the madder dyeing which had already reached its zenith. And this reform materialized. Far-sighted dyers and colorists participated in it. No body questioned (*as later with regard to the artificial Indigo*) about the price of the new product but much more important seemed the simplification, acceleration and raising of the industries dependent on its application.

At first the artificial Alizarine penetrated into the dyeing and printing of cotton. Here was the weakest point of madder, of its extracts and of its preparations, the *Garancine*. Very soon the first blue and yellow tinted commercial products were

followed by much more improved, purer and cheaper prices derived from the quickly developed technique of sulphonation and alkali fusion. Through the discovery of the Turkey Red oil, through the introduction of continuous dyeing and steaming methods, application after application was torn away from the natural product. The attack was supported by new confederates. At first in 1874, de Lalande, obtained the artificial purpurine by the oxidation of Alizarine with arsenic acid and other oxidising agents. (*de Lalande, Engl. Pat.* 1874, *No.* 2841). Then Strobel, an Alsatian colourist observed that the red alum lake of Alizarine was converted on the fibre into a stable yellowish red by nitrous vapour; Rosenstiehl (*Rosenstiehl, Ber.* 9, 1036) discovered in this process the formation of nitroalizarine whilst thereupon the dye industry immediately established the direct nitration of Alizarine to the Alizarine orange (*Engl. Pat. H. Caro,* 1876, *No.* 1229; *Schunk and Roemer, Ber.* 12, 583, 1003). The dyestuff formed by the nitration of Alizarine in sulphuric acid solution is not yet clear. From it was derived Purpurine and by reduction the Alizarinemaroon (*Bad. Anil. Sodaf,* 1885, *R. Bohn*). In previous nitration experiments Strecker (*Zeitschr. f. Chem.* . 1863, 263) came across a nitro-oxyalizarine and Perkin (*Perkin, Ber.* 8, 780) found the isomeric α nitroalizarine starting from diacetyl Alizarine. But first in the spring of 1876 when Alizarine Orange came into the market, Alizarine, flavo and anthrapurpurine (*Schunk and Roemer, Ber.* 2, 682; *Perkin, Ber.* 6, 149) were joined by a new ally whose derivatives Alizarine Blue [*Bad. Anil. Sodaf.* 1878 (*H. Brunck*); *Graebe, Ber.* 9, 522, 1646; 12, 1416; *Ann. d. Chem.* 201, 533] with its latest descendants " Alizarine Green " [*Alizarine Green, -blue green, -indigo blue Bad. Anil. Sodaf.* (*R. Bohn*), D.R.P. 1888, *No.* 46654; *Graebe, Ber.* 23, 3739; 24, 2297] and a series of analogously formed anthraquinone compounds rich in hydroxyl groups [*Alizarine Cyanine-Bordeaux etc. Elberfelder dye factory,* D.R.P. 1891, *No.* 60855; *R. Schmidt, J.f. prakt, Chem.* 43, 237; *Gattermann, do.* 43, 246] combined with the synthetically produced Anthragallol (*anthracene brown, Bad. Anil. Sodaf.* 1886 *R. Bohn, Seuberlich, Ber.* 10, 38) were following the battle in its further

course. From the last experiments resulted the valuable Anthracene Blue (*Bad. Anil. Sodaf.* 1891, *R. Bohn*).

Also from other groups similar mordant dyes joined, first Baeyer's Galleine and Coeruleine, the first fast green dyestuff, then the Galloflavine (*Bad. Anil. Sodaf. R. Bohn, D.R.P.* 1886 *No.* 37934; *Bohn and Graebe, Ber.* 20, 2327), and Gallocyanine (*Horace Koechlin, D.R.P.* 1881 *No.* 19580; *Nietzki and Otto, Ber.* 21, 1740), Roussin's Naphthazarine and later yet another series of yellow and other colouring oxyketones (*Alizarine yellow, Bad. Anil. Sodaf. R. Bohn D.R.P.* 1889 *No.* 49149; *Graebe and Aichengrün, Ber.* 24, 967) and azo-dyestuffs. To the assemblage of these new products Methylene Blue was soon added. The calico printing was supplied in quick succession with an unexpected gallaxy of colours of great and easy applicability. In place of the unstable steam-, application- and pigment dyes of former times there came light- and water-fast shades. No more had one to ' illumine ' by hand with unstable dyes the madder lakes produced by a tedious dyeing process. Multicoloured patterns were printed simultaneously by machinery. Then they were fixed in steam. The insolubility of Coeruleine (*Horace Koechlin, Bull. Soc. Ind. Rouen* 1876, 586), Alizarine Blue (*Bad. Anil. Sodaf. H. Brunck, D.R.P.* 1881 *No.* 17695; *Brunck and Graebe Ber.* 15, 1783), Naphthazarine (*Bad. Anil. Sodaf. R. Bohn D.R.P.* 1887 *No.* 41518) and the temporarily used Azarine (*Höchster Dye Firm, A. Spiegel, D.R.P.* 1883 *No.* 29067; *Spiegel, Ber.* 18, 1479), the tendency of the lake forming dyes to combine with the metallic mordants already in the print dyes was overcome by their conversion into decomposable bisulphite-compounds. One improved the previously used mordants and recognized chiefly the high value of chrome mordants to which little attention had been paid before.

The centre of this movement was formed by the artificial Alizarine, whose rapidly sinking market prices—the consequence of an unprecedented struggle of competition and tough, rational work—also unobstructedly overflanked the economical significance of madder cultivation. Fast dyes were now produced at much cheaper cost and thereby their use rapidly surpassed the former limits. The textile industry gained a greater development, trade

and commerce took more extensive courses. Other effects were still manifested by this movement. The prejudice against the fastness of the coal-tar dyes, called forth by the aniline dyes was broken. Not only to the madder but also to the Indigo and to the wood dye equal, nay even superior opponents had arisen, and the aim of the industry was clearly disclosed. The displacement of the natural products by better, cheaper and more easily applicable substances ensued.

At the time of the World Exhibition in Viena in 1873 [*Graebe and Liebermann—Das künstliche Alizarin (Vieweg)* 1876, 36] the then annual production of artificial Alizarine corresponded already to the previous demand of madder dyestuff, five years later at the World Exhibition in Paris Reverdin and Noelting' could report that the French madder cultivation had fallen to $\frac{1}{50}$th of its previous output and that it did no longer pay.

From 1878 artificial Alizarine, its derivatives and attendants flooded the conservative domain of wool and piece dyeing, which was little affected up to the time. Here not only the highest claim on light and milling was being asked but a system of dyestuffs (*this systematic introduction of Alizarine dyes in the wool dyeing is due to the Badische Anilin und Sodafabrik—H. Brunck*) of mordant and dyeing methods had to be created by which safe and simultaneous production of mixed tones of every description from bright grey to yellow, to madder red, to indigo blue, to green, to brown, and to the deepest fast black were guaranteed. Also here the revolution was slowly completed. Sulphoacids of Alizarine [*Prizbram & Co. D.R.P. No.* 3565 (1878) ; *v. Perger, Journ. f. prakt. Chem.* 18, 173; *Graebe and Liebermann, Ann. d. Chem.* 160, 144; *Graebe, Ber.* 12, 571] and its derivatives and the mordant dyes of azo-group (*Alizarine Yellow etc. Nietzki, D.R.P. No.* 44170 *and other salicylic acid dyes—followed Carbazole Yellow and so forth*), one improved and investigated incessantly on small and large scales, and gradually, even by the army cloth dyers the knowledge of the higher value of the artificial dyestuffs was recognized. Thereby the first fight against the Alizarine and Purpurine was conclusively decided. The vegetable dyestuffs retired to the last fortifications of the paint-

ing colours and the isolated applications in wool dyeing. Wheat fields waved anew in the country-side where once the madder plants had bloomed.

During this conclusive fight the strictest reciprocal action had, as always, ruled between theory and practice. The dyer and the colourist stepped by the side of the dye technician and jointly they offered their experiences to Science. A rich litera-thre grew up in the entire domain. The structure and synthesis -of the anthracene derivitives were completely established. How-ever, the investigation still surpassed these aims.

Scarcely had Alizarine Orange appeared in the market when a remarkable trend of ideas caused the colorist Maurice Prudhomme to heat this dyestuff with a mixture of glycerine and sulphuric acid at about 200°C (*Bull. Soc. Ind. Mulh.* 1877). From the reaction product he isolated a blue indigo-like substance which coloured the alum mordant violet,—the later Alizarine Blue. To make out the constitution of Alizarine Blue Graebe seized again Baeyer's approved method of the zinc dust distilla-tion, (*Graebe, Ber.* 12, 1416) but as mother substance of the dyestuff he did not get a hydrocarbon but a base: the anthra-quinoline, which bore to anthracene the same relation as quinoline to benzene. The formation of this base reminded him of Koenig's synthesis of quinoline just discovered from alkyl aniline (*Königs, Ber.* 12, 453) and thus the significance of nitro-compounds and of glycerine for the reaction was realized by him. This finding led in the next year, 1880 to Skraup's quinoline synthesis from aniline, nitro-benzene, glycerine and sulphuric acid, which became the starting point for the branching off from the dyestuff industry of the artificial medicaments.

So we return here again, so to say, to the origin of our industry—to the synthesis of quinine from allyltoluidine, once dreamed of by Perkin and we think once more of Leibig's pro-phetic words that quinine as well as morphine would be produced from coal-tar!

Let us now turn to another branch of industry resulting out of Baeyer's investigations.

In pursuance of his fundamental theoretical conception (*Baeyer, Ber.* 3, 63). "On the Water-elimination and its

Significance for Plant-life and Fermentation", and stimulated by
the investigations of Franz Reim (*Reim, Ber.* 4, 329) on the
haemotoxylin Baeyer heated (*Baeyer, Ber.* 4, 457) pyrogallic
acid with phthalic anhydride in 1871 and obtained a dyestuff,
the Galleine, which coloured iron and aluminium mordants
similarly as did red and blue wood, and with reducing agents
like haematein it is also transformed into a colourless substance,
the Gallin. Further experiments showed (*Baeyer, Ber.* 4, 555)
that by heating with sulphuric acid Galleine is transformed into
a new dyestuff, the Coeruleine which colours the aluminium
mordant green and by alkaline reduction forms an indigo-like vat
dye. He was reminded of the Chinese Lo-Kao green. Phthalic
anhydride also reacted with resorcin forming yellow coloured
Fluorescein possessing a brilliant green fluorescene. By a closer
study of these reactions (*Baeyer Ber.* 4, 658) which take a more
or less similar course with the substitution of phthalic acid by a
series of other substances—among which phthalic acid chloride,
bitter almond oil, acetone and succinic anhydride—and which can
be observed also by the use of phenol, hydroquinone, pyrocatechol,
phloroglucin and α-naphthol, it was proved that phthalic acid
and its substitutes had acted not merely as water eliminating
agent, but as 'binding substances' for the 'chromogen', phenols
into the synthesis of the dyestuff molecule. Also Kolbe-
Schmitt's synthesis of the Rosolic Acid from phenol, sulphuric
acid and oxalic acid allowed now a similar interpretation through
the binding action of the carbonic acid. The colour-phenomena
and their disappearance by reduction lead to a 'quinone like'
grouping in the dye compound.

So, these first communications of Baeyer lead us over the
phenol dyestuffs, of compounds discovered by him, to a new
interminable field of dyestuff synthesis. New points of view,
new materials, new methods were opened up for further investi-
gations. The previously investigated group of phthaleins is
formed by the 'succineins' and related groups; synthesis with
aliphatic and aromatic acid anhydrides, acid chlorides, aldehydes
and ketones appeared here in the beginning. From the phenol
dyes we look to the neighbouring domain of the rosanilines.

And nevertheless years had to pass before these investiga-

tions came to practical life. The artificial Alizarine absorbed the industrial interest; the new reagents were laboratory preparations and therefore too costly for the synthesis of the wood dye-like substances.

Then in the spring of 1874 there appeared quite a peculiar dyestuff, the Eosine (*Bad. Anil. Sodaf. H. Caro, Ber. 7*, 1743). It dyed without mordant in an acid bath, the outstanding beautiful hues flouresce on the fibre and increase from the softest shades of dawn to the illuminating red of the Cochineal. In spite of its enormously high price (initially 800 marks per kilo) it at once found its entrance in the silk dyeing. The delicate rose colour, glimmering in a yellowish lustre, earned at once the favour of the fairsex who determine the fashion. Then the muslin print took possession of it, the preparation of artificial flowers, also the cotton and paper dyeing succeeded in obtaining a rose colour of the saffron-like shade. Soon the initial price fell and the applications multiplied, new market products of bulish shades followed, one dyed and printed on wool and silk up to the richest scarlet tones.

Still the German patent law was missing; even in foreign countries the Eosine was not protected, however, its origin could not be hidden for long. Hofmann solved the problem (*Ber.* 8, 66; *Baeyer, Ber.* 8, 146) in the beginning of the following year, here also he fell back to the zinc dust reaction and obtained rich yield of benzene. Further investigations disclosed Eosine to be a tetrabromo-derivative of Baeyer's Fluorescein, from which it was derived by direct bromination.

Thereby, it was simultaneously realised, that a new element had been introduced to the dyestuff technique; the raising of the colour tone in the direction from yellow to red being attained by halogen substitution. Up to then one knew only of a similar acion of the alkyls, phenyl, tolyl and benzyl. By the introduction of the nitro-group arose, as a rule, yellow colouring substances, by sulphonation, the spirit-soluble dyestuff became water-soluble. But one had not yet noticed the diversity conditioned by position. Now one found that chlorine, bromine or iodine apparently in proportion to the increase in the weight of the molecule caused by its entrance, produces a series of Eosines

from yellowish to bluish tinges of which many became prized commercial articles. Also the nitro-group associated with bromine, one alkylates and benzylates then adds the halogen (*Noelting* 1875, *Eosine from dichlorophthalic acid*) and subsequently also, nitro, amino, oxy (*Baeyer, Ber.* 10, 1082) and sulpho-groups (*Graebe, Ber.* 18, 1126) to the phthalic acid used for the synthesis. The experiences gained here have since been utilized in other dyestuff groups. Thus Baeyer's phenol-dyes have entered practical life at first with Fluorescein, soon one was reminded of Galleine and Coeruleine and prepared gallic and pyrogallic acids in the factories which on their part again later proved indispensable for the preparation of other mordant dyes. For they also contained hydroxyl groups in the contiguous "alizarine position" and the gallic acid besides being a "binding substance" had an easily combining carboxyl group.

The technical impulse manifested again its inevitable reaction on the chemical investigation. Touched by the fingers of 'Eos' the phthaleins awoke to new life. Since his first communications Baeyer had turned mainly to the condensations of aldehydes with phenol and hydrocarbons and thereby discovered the formation of diphenyl methane by means of formaldehyde, which has become so important in recent times (*Baeyer, Ber.* 5, 1094; 6, 220), while much earlier diphenylmethane had been obtained by Zinke (*Zinke, Ber.* 4, 298) from benzene and benzyl chloride and later by Victor Meyer (*Meyer and Würster, Ber.* 6, 963) from benzene and benzyl alcohol. In the course of these investigations, in the condensation of benzene and benzhydrol (*Hemilian, Ber.* 7, 1203) a new synthesis of triphenylmethane was found which had been produced first by Kekulé and Franchimont (*Ber.* 5, 906). From it triphenylcarbinol was obtained by oxidation. However, the trinitroderivative of triphenylmethane was now reduced and then oxidized, and it was only after several years that its significance was to be fully disclosed. These investigations formed the foundation for the later dyestuff synthesis in the di—and triphenylmethane groups. Of the Phthaleins only the phthalein of hydroquinone (*Grimm, Baeyer, Ber.* 6, 506) had been exhaustively described. Before the discovery of Eosine the Fluorescein presented the still incom-

plete maiden investigation of Baeyer's student Emil Fischer (*Ber.* **7**, 1211).

However, a new important result emerged from the works on Hydroquinone Phthalein. As a scanty by-product the quinizarine, a coloured substance of the composition of Alizarine was obtained. By heating with zinc dust, anthracene was found to be its mother substance. Both the neighbouring carbonyl groups of the phthalic anhydride by forming anthraquinone had ~~taken~~ hold of a benzene residue; hydroxyls had taken up the hydroquinone position in it; to Fittig's conception that anthraquinone was a double ketone (*Fittig, Ber.* 6, 167) a further proof had been adduced. Much earlier isolated synthesis of anthraquinone and oxyanthraquinone from benzoic acid (*Kekule and Franchimont, Ber.* 5. 909) and oxybenzoic acid (*Barth and Senhofer* (*Anthrachryson, Anthraflavon*) *Ann. d. Chem.* 164, 109. 170, 100. *Jaffe, (Rufigallic acid) Ber.* 3, 694] have pointed to it; zinc dust distillation method has always led to their perception. Now Baeyer (*Baeyer and Caro, Ber.* 7, 968; *Ber.* 8, 152) through his discovery of Quinizarine was led to a systematic synthesis of anthraquinone derivatives from benzene derivatives and phthalic acid", and thereby to a fruitful knowledge of the sructure of Alizarine, Purpurine and Quinizarine.

With the Eosines Baeyer now began a new fundamental and thorough investigation in the domain of Phthalein, the results of which have been laid down in a series of exhaustive papers from the year 1876 to 1882 [*Baeyer, Annal d. Chem.* 183, 1; 202, 36, 153; 212, 340. *Buchka (Galleine, Coeruleine, Ibid* 209, 249]. On the essential points his work was accomplished in 1880, the constitution of the Phthaleins and their kindred relations to the groups of Rosaniline and anthracene dyestauffs have been made definitely clear.

In a rough sketch the following result is presented :

The mother substance of Phenolphthalein is the phthalophenone of Friedel & Crafts, produced according to their wonderful aluminium chloride synthesis out of phthalyl chloride and benzene. The phthalophenone, however, is not the supposed double ketone. By taking up water, the ortho-carboxylic acid of triphenylcarbinol results from it which is stable in alkaline

solution only and from which, by reduction, the corresponding acid of the triphenylmethane and through the final splitting up of carbonic acid the triphenylmethane itself are obtained.

Phthalophenone is therefore a lactone (*Fittig, Ann. d. Chem.* 200, 62). It is diphenylphthalide, the doubly phenylated derivative of the phthalide (*Hessert, Ber.* 11, 237) formerly taken for phthalaldehyde. From this mother substance a dioxydiphenylphthalide was obtained now by nitration, amination and exchange of the amino group by hydroxyl, which has been proved to be identical with Phenolphthalein. In the alkali fusion by absorbing water it decomposed into benzoic acid and paradioxybenzophenone, the latter by further heating into paraoxybenzoic acid and phenol, and finally completely into phenol and carbonic acid. In the formation of Phthalein only one methane carbon atom of the phthalic acid attacked therefore 2 phenol molecules and indeed into the para positions of their hydroxyl groups.

On the other hand phenolphthalein is the leuco-compound of the phthalein, a corresponding dioxy-derivative of the triphenylmethanecarboxylic acid and participates with the latter, its mtoher substance, the property to be converted into substances of the anthracene series by the action of dehydrating agents. From the triphenylmethane carboxylic acid is derived a phenyl derivative of Lierbermann's anthranol by the treatment with sulphuric acid (*Liebermann's reduction experiments in the anthraquinone series. Ann. d. Chem.* 212, 1). By heating with zinc dust phenylanthranol furnished its mother substance, the phenyl anthracene; by oxidation: phenyloxanthranol corresponding to the anthraquinone. In an analogous way from phenolphthalein are formed the phthalidine and phthalideine, the dioxyderivatives of phenylanthranol and phenyloxanthranol.

Now one also recognized that Coeruleine owed its origin to an anthracene condensation of that kind. Starting from Galleine one reached Coeruleine in a similar way as from phenolphthalein to phenofphthalideine. Heated with zinc dust the dyestuff furnished its mother substance: the phenylanthracene; like the phthalideine it is a derivative of phenyloxanthranol. However, it does not contain unimpaired hydroxyl groups of the pyrogallol used for its synthesis. Already in the formation of

Galleine an anhydride-like combination resulted between the two pyrogallol residues by the elimination of water, and besides this by simultaneous oxidation of one of each of the hydroxyls, a quinone group was formed, as in the case of Cedriret investigated by Liebermann and Hofmann (*Liebermann, Ann. d. Chem.* 169, 22; *Hofmann, Ber.* 11, 329). By the conversion of Galleine into Coeruleine these oxygen groupings now remain intact; there appeared, however, by the elimination of water a further oxygen bond similar to that of the Rosolic Acid between a carbon atom of the binding carbon groups and a pyrogallol-residue. Accordingly the mordant dye Coeruleine contained only one hydroxyl, but in a contiguous position to the quinone group.

The anhydride formation in Galleine is not a solitary instance. Already in the preparation of Phenolphthalein Baeyer had found a by-product insoluble in alkalis, the phenolphthalein anhydride. By the substitution of phenol by parachlorophenol or paracresol such an anhydride was obtained as the principal product and Fluorescein proved to be a dioxy-derivative of phenolphthalein anhydride. In recent times Richard Meyer, (*Ber.* 24, 1412) made it probable that the formation of this anhydride rests on the entrance of the interconnected methane carbon atom into contiguous position of the phenolhydroxyl group and that the so formed six membered ring closed by an oxygen atom, is the carrier of the characteristic properties of the fluorescein group. In a stricter sense the mother substance of this group was therefore, the phenolphthalein anhydride. Its sulphuric acid solution shows green fluorescence. A similar ring formation had already been recognized in the diphenylene ketone oxide or the xanthone which Graebe (*Graebe, Ann. d. Chem.* 254, 265) proved as the mother substance of the euxanthone group, and to which "Indian Yellow", probably also the Galloflavine arising from the gallic acid by moderated oxidation belong. If one thinks of replacing the ring closing oxygen atom in diphenyleneketoneoxide by a carboxyl group, one comes again to the atom grouping of anthraquinone. In an equally strict sense of the word, the latter, and not anthracene was to be the mother substance of the Alizarine dyes.

So we see, how from Baeyer's investigations gradually and

frequently actively supported by his method of zinc dust distilla-
tion definite views on the mother substances of our dyestuff
groups have been developed. There appear formations partly
open and partly of cyclic structures. Let us follow a little
further on the course of this development and let us enter the
domain of the Rosaniline.

Here, the impulse was given by the first investigations of
Hofmann in conjunction with the first knowledge of toluene as
methyl benzene. From Hofmann's discovery of the diazo-com.
pound of Rosaniline, which in consequence of an accidental
observation in a manufacturing experiment with dinitronaphthol
—was obtained in the form of its chromic acid compound, a
nitrogen- free phenol according to the method of Griess by de-
composition with water. Its characteristic properties eventually
claimed it as Rosolic Acid and expressed its relations to Rosaniline
through formulae (*Caro and Wanklyn, Proc. Roy. Soc.* (1866)
15, 210). Soon afterwards, with reference to Hofmann's
explanations on the formation of Rosaniline from a mixture of
pure aniline and paratoluidine in the oxidative fusion, an
analogous formation of Rosolic Acid from a mixture of pure
phenol and paracresol was observed, besides, also the formation
from phenol by heating with substances of the aliphatic series,
particularly with iodoform. This led on the one hand to the
explanation of the formation of dyestuff in the oxidative fusions
by the binding action of methyl residues, and on the otherhand
to understand the synthesis of a dyestuff from pure phenol and
oxalic acid in the Rosolic Acid process of Kolbe and Schmitt.
The opinion was expressed: That the dyestuff acid and the
dyestuff base are members of the same family, that at the basis
of both the same hydrocarbon skeleton was lying (*H. Caro, Phil.
Mag.* 32, 126).

Which was then this hydrocarbon? According to Griess'
method it could not be obtained from the diazo-compound of
Rosaniline. Always a blue dyestuff was formed (*Caro, Franz,
Brev.* 1866, 72732). In 1873 Graebe started the investigation
of the Rosolic Acid (*Graebe and Caro, Ber.* 6, 1390; *Ann. d.
Chem.* 179, 184). In the meantime Dale and Schorlemmer
(*Dale and Schorlemmer, Ann. d. Chem.* 166, 279; 196, 75) had

begun work on Kolbe and Schmitt's commercial product—the
yellow Coralline or "Aurine" and had confirmed its formation
from pure phenol. Graebe recognized the formula of Rosolic
Acid derived from Hofmann's Rosaniline formula with 20 atoms
of carbon as the correct one; the same number was found in
Aurine by Dale and Schorlemmer and since there was no reason
to suppose the existence of dyestuffs poorer in carbon atoms, or
a different way of action of both the toluidine molecule in the
fuchsine melt,—so, in the mother substance of Rosaniline and
Rosolic Acid just as in the phthaleins a chain of three
benzene rings closed by two methane carbon atoms had to be
accepted. The leuco-compounds of the dyestuffs possessed the
proved character of triamino and trioxy derivatives, their con-
version into coloured condition by elimination of water was
explained by the resulting 'quinone like' bond of each of the
two amino groups or of the oxygen atoms. With this conception
the composition of Iodine Violet and Iodine Green ascertained
by Hofmann and Girard stood harmonised. The formation of
Methyl Violet from pure dimethyl aniline appeared then as an
aldehyde condensation of formaldehyde formed by the oxidation
of the split up methyl group. In course of these investigations,
however, never a Rosolic Acid completely identical with Aurine
could be obtained from a commercial Fuchsine—such a product
could only be had from the Aniline Red of Hofmann and
Rosenstiehl produced by means of pure aniline and para toluidine
(*Rosenstiehl, Zeitschr. f. Chem.* 1869, 192).

A complete explanation could also given here only by the
preparation of the mother substance and its regeneration into
the dyestuff. This keystone was inaugerated by the brilliant dis-
coveries of Baeyer's students Emil and Otto Fischer (*Emil and
Otto Fischer, Ber.* 9, 891 ; *Ann. d. Chem.* 194, 242).

Starting from the diazo-compound of leuco aniline prepared
from commercial Fuchsine, they obtained in 1876 a hydrocarbon,
$C_{20}H_{18}$ to which no significance was attached at first. It is
different from the well-known dibenzylbenzene; on oxidation it
takes up an atom of oxygen.

In the following year Dale and Schorlemmer (*Dale and
Schorlemmer, Ber.* 10, 1016) discovered the conversion of Aurine
into Rosaniline by heating with ammonia.

8

When Emil and Otto Fischer took up again their investigations in 1878 with pure pararosaniline prepared from commercial aniline and paratoluidine (*Emil and Otto Fischer, Ber,* 11, 195, 473) as well as shortly afterwards with the Rosaniline prepared from Aurine, they obtained in the same way as before a hydrocarbon. Its analysis gave, however, the surprising formula $C_{19}H_{16}$, which was immediately proved to be identical with the well-known triphenyl methane; its oxidation product is the triphenyl carbinol. its tri-amino derivative, the para leuco aniline, by careful oxidation of which the original dyestuff is regenerated. Now also the hydrocarbon of commercial Fuchsine found its significance as tolyldiphenyl methane and the dyestuff itself as the next higher homologue of the simplest rosaniline of the formula $C_{19}H_{17}N_3$.

Accordingly triphenylmethane appears as the mother substance of the rosaniline group, its trihydroxy derivative is the leucoaurine, whose next higher homologue is the leucorosolic acid.

Still there were many questions to be solved regarding the constitution of the colouring substances. How did they originate from the colourless leuco-compounds, how were the coloured anhydrous rosaniline salts transformed into the colourless hydrated bases? How can one explain the formation of a normal diazo-compound from the Rosaniline and the colourless hydrocyan compounds of the dyestuff? (*Hugo Müller, Chem. News,* 1866, 13, 135).

To clear up this point Emil and Otto Fischer had assumed the dyestuffs as triamino and trioxy-derivatives of a hydrocarbon, poorer in hydrogen, the diphenylmethane, and in the instability of its ' phenylene bond ' they recognized an unconstrained significance of the transformation into the colourless condition. In the mean time the existence of phenylene compounds had, however, become unstable and thereby the constitution of the dyestuffs appeared anew as an open question (*Emil & Otto Fischer, Ber.* 11, 612).

To answer this question Graebe appeared again (*Caro and Graebe, Ber.* 11, 1116). The original quinone formulae were put

aside. The anhydrous base was now recognized as the tri-amino compound of the tri-phenyl carbinol. The colouration of its anhydrous salt resulted from the ring-closure completed through water elimination between the hydroxyl and an amino-group by an arrangement of hydrogen, hydrocyan or sulphurous acid (*in _lurinc, containing the corresponding carbon-oxygen linking also from acetic anhydride*) this colour producing bond is again ruptured. This results in the elimination of hydrogen by the conversion of the anhydrous leuco-compound into the dye-stuffs and it is retained by the diazotization of the aniline red.

Simultaneously Emil and Otto Fischer came to the same opinion regarding the constitution of the dyestuffs. They made the brilliant and decisive experiment. They oxidized the already known trinitro-triphenylmethane into trinitro-triphenylcarbinol and they added zinc dust to its acetic acid solution. At once the splendid colour of fuchsine appeared!

But they explained the diazo-compound of the pararosaniline as a normal tridiazoderivative of the triphenylcarbinol. The gold salts contained water. So a fission of the carbon nitrogen bond of the dyestuff takes place by the diazotisation with the addition of water.

The " mother substance " of the triphenylmethane dyestuff in the strict sense of the term, is therefore, the triphenyl-carbinol and only for its leuco-compound, the triphenylmethane. Besides this in the coloured compounds reigns a peculiar atomic grouping, a colour carrier " chromophore " (*Otto N. Witt, Ber.* 9, 522). Finally the influence of homology and isomerism in the side chains and the number, position and substitution in their salt-forming oxy and amino groups gained an weight by its derivatives. Much was already known, now it could be arranged under uniform view points with surprising quickness. One could foresee new things. Also the Phthaleins and the dyestuffs formed from phenol and tertiary aromatic amines joined the triphenylmethane groups very soon. Out of the knowledge of constitution the synthesis of dyestuffs developed systematically.

At first it was still the question to get an insight into the position of the oxy and amino groups with respect to the linking

carbon atoms. For one of these groups one knew the position from the formation of Pararosaniline and Aurine and one also knew that pure paratoluidine or paracresol could produce neither Fuchsine nor Rosolic Acid. The stepwise degradation of the dyestuffs to its components and their re-building from them furnished a further insight.

Much earlier it has been observed that from Rosaniline (*Liebermann, Ber.* 5, 144; *Ber.* 6, 951) and Rosolic Acid (*Graebe and Caro, Ber.* 6, 1392) by heating with water at high temperature colourless compounds emerged. Finally besides phenol a nitrogen-free substance originated from Rosaniline. This compound received its significance however, when only the product obtained by Staedel (*Staedel, Ann. d. Chem.* 194, 307) was recognized as paradioxybenzophenone and by heating it with phosphorus trichloride and phenol the dyestuff could be regenerated (*Caro and Graebe, Ber.* 11, 1348). So it was proved not only probable that two of the salt-forming groups in the dyestuffs should occupy the para position to the methane carbon atoms—for the second and third it has been confirmed only later (*Emil and Otto Fischer, Ber.* 13, 2207)—but it was, as indeed it had happened shortly before, that by the potash fusion of Phenolphthalein a further light was thrown also on the decomposition and synthesis of the triphenylmethane dyestuffs.

In the case of Aurine one came downwards from carbinol to ketone, to carboxylic acid and finally to phenol and carbonic acid. Therefore the carbonic acid in one or the other of its active forms appeared as the " binding substance " already assumed by Baeyer. One can rise upwards from every step to the next higher one. The methods were established partly through numerous experiments, partly they were apparent. Kolbe's salicylic acid synthesis formed the starting point. In a similar way the basic dyestuffs could be built up and it was anticipated that not only the same phenol and amine but also building units of different kinds can in this way unite in pairs with one another. Five years later this expectation was completely fulfilled by the synthesis of phosgene-dyestuffs.

In the meantime industry and science had wandered from Phthalein to the field of triphenylmethane, from phenol dyestuffs

back again to the aniline dyes derived from tertiary aromatic amines. Hofmann and Baeyer's schools met here in competition.

Reimer Tiemann Synthesis :

Up to 1874, till the discovery of nitrosodimethylaniline and nitrosophenol a convincing conception for the analogous behaviour of tertiary aromatic bases and phenols in the synthetic reactions had been missing. In the very same year Tiemann and Haarmann (*Tiemann and Haarmann, Ber. 7*, 608) succeeded in converting coniferin to vanillin in Hofmann's laboratory. At once prospects opened for the synthetic processes for the artificial vanillin from aromatic aldehydes, and in pursuance of the works, Reimer and Tiemann discovered in 1876 (*Reimer, Ber. 9*, 423; *Reimer and Teimann, Ber. 9*, 824, 1285) the synthesis of salicyl aldehyde and para-oxybenzaldehyde and of the corresponding acids by the action of chloroform and carbontetrachloride respectively on phenol in alkaline solution. Simultaneously Michler (*Michler, Ber. 9*, 400, 716, 1899), a student of Baeyer's student Victor Meyer, investigated in the laboratory of the Technical High School at Zurich the action of carbonyl chlordie on dimethylaniline. He obtained the chloride of the para-dimethylaminobenzoic acid, therefrom the acid or, by heating with dimethylaniline, the tetramethyldiaminobenzophenone and then from this the tetramethyldiaminobenzhydrol. Diethylaniline gave analogous results, and benzoyl chloride had already been drawn into the field of investigations.

Once again, almost at the same time Hofmann's students Doebner and Stackmann (*Doebner and Stackmann Ber. 9*, 1918) were led to a deduction from Reimer's synthesis. Instead of chloroform they allowed 'phenylchloroform,' the benzotrichloride to react with phenol. In the presence of zinc oxide combined with hydrochloric acid, para-oxybenzophenone or 'benzoylphenol' is formed; without zinc oxide, however, a reddish brown resinous product results. The Rosolic Acid-like dyestuff contained therein (*Caro & Graebe, Ber. 11*, 1351), the present benzaurine or phenol benzein was later built up simultaneously with Aurine from oxy-benzophenone by heating with phenol and phosphorus trichloride and Doebner (*Doebner, Ber. 12, 1462; Ann. d. Chem.,*

217, 223; 257, 70) correspondingly referred to it as a dioxyderivative of triphenylcarbinol, but he did not assume therein the anhydride linking of the Aurine. In the potash fusion the dyestuff decomposed into para-dioxybenzophenone and benzene. The benzotrichloride, therefore, had interlocked with its methane carbon atom two phenol molecules analogous to the previously explained phthalein-formation (*Baeyer, Ber.* 12, 642). In clear knowledge of the 'similar behaviour of phenol and tertiary aromatic amines Otto Fischer shortly after Michler had on the other hand (*Otto Fischer, Ber.* 9, 1753; *Ann. d. Chem.* 206, 83) begun investigation on the phthalein of tertiary aromatic bases, and already in 1876 he had shown that dimethyl-aniline, with reference to the phthalein reaction, behaves exactly as phenol. With phthalyl chloride a green dye-stuff was derived but not of the same quality as Methyl Green. Then his investigation advanced further to reaction with other acid chlorides and tertiary bases. The similarity with the condensation products of phenols shown throughout, led him (*Otto Fischer, Ber.* 10, 952, 1623) during the next year to examine more closely the aldehydes already tried by Baeyer in his discovery of phenoldyestuff, particularly the bitter almond oil in its behaviour towards dimethylaniline. As expected, benzaldehyde also attacked two molecules of tertiary amine, a colourless base was formed with the help of zinc chloride whose salt was oxidized quickly, particularly in alcoholic solution, to a beautiful bluish green dyestuff. The bitter almond oil green or Malachite Green was discovered! However, the utilization of the scientific discovery was still missing. The costly bitter almond oil was known only in perfumery, the oxidation of the leuco-base could obviously not appear according to the process of the leuco-aniline as a technically feasible operation. In the first months of the year 1878 Malachite Green appeared in the market. In colouring power and stability it proved superior to Methyl Green—the coloured fibre can be heated strongly without turning the green to violet. And when the announcement of its patent was known (*Act. Ges. für Anilf. Berlin,* D.R.P. 4322, 26th *Feb.*, 1878)—it was the first of a basic rosaniline dyestuff under the authority of the German Patent law—one learned that the valuable foreign product had
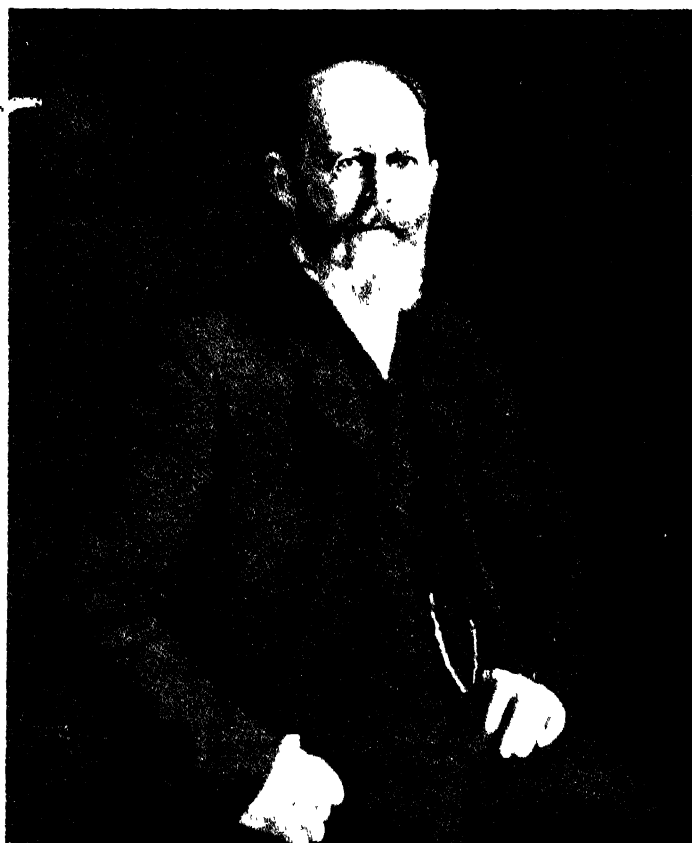
EMIL FISCHER (1852–1919)

EMIL FISCHER

1852—1919

Emil Fischer was born in a small district town Euskirchen, Germany, on the 9th October, 1852. He was the youngest of the eight children of his parents. His father Laurenz Fischer, who carried on some small scale business, was a man of unbounded energy and where difficulties arose he proved himself to be a master of practical self-help. The establishment of a dyehouse in the Wisskirchen close to his native town and an experimental dyehouse in Euskirchen had an influence on the choice of profession of young Emil. For Laurenz Fischer often thought that if any of his sons studied Chemistry he might be in a position to cope with the difficulties that were frequently met with in the conduct of the firm of the Fischer-Brothers. The participation in the enterprise of iron and cement industry and its successful running also served to increase Fischer's father's great inclination for Chemistry.

Young Emil passed his Matriculation examination in 1869 from the Gymnasium at Bonn. He grasped everything quickly and had a special knack for mathematics. The serious question of choice of career came in 1869. Emil strove to become a mathematician and physicist but his father disliked the idea as being too abstract. A short experiment was made to turn him into a businessman to look after their firm but the father was soon convinced that Emil was too dull for the profession. And thus the choice finally fell on Chemistry. At Bonn Kekulé's laboratory could offer him no charm so he went to Strassburg where Adolf Baeyer's inspiration inflamed in young Emil's mind a strong love for Organic Chemistry. From the beginning Fischer showed an extraordinary skill for experimental work and an aversion for putting up theories and hypothesis. Emil Fischer obtained his doctorate degree from the University of Strassburg on his work on Fluorescein and Orcinphthalein. But soon he turned his attention to the elucidation of the more complicated substances of biochemical significance. In 1878 Fischer discovered phenylhydrazine which proved an invaluable reagent in his brilliant researches on sugars. Gradually he penetrated into the more complex problems of purines, proteins, tannins and enzymes. Whatever Fischer has touched, he has brought light and order there. In 1892 he was appointed Professor of Chemistry in the Berlin University, and he continued to hold this post to the last day of his life.

Fischer obtained the Nobel Prize for his pioneering work on sugar and purine groups. While receiving the prize from the hands of the King Gustav of Sweden in the magnificent Hall of Stockholm Music Academy on the 10th December, 1902, just two months after his father's death, the president said, " The peculiar nature of investigation which has characterized organic Chemistry during the last decade, has attained its highest perfection and finest shape in Fischer's sugar and purine synthesis. Considered from the experimental point of view they are really unsurpassable." Fischer's works on the Chemistry of proteins is another

masterpiece of experimental efficiency. The following extract from his biography is worth quoting in this connection. 'Of Tolstoy once a critic remarked, "It is easier to establish a new religion than to write a book like ' Anna Karenina.' And in the same sense it appears much less difficult a task to propound a scientific theory than to investigate the constitution of proteins and to attain synthetic successes in the line."

About industry and original research Fischer held the view that a young chemist who will dedicate himself seriously to the pursuit of science should keep his hand fundamentally from off any invention. For, scientific work demands, if it is to lead to any noticeable success, the whole-hearted devotion, and endures not the strong deviation as to which invention, patent and their utilization will bring him any positive gain. A proof of this he embodied in his own character. In his younger years he was offered the post of the director of the principal laboratory of the Badische Anilin und Soda Fabrik in Ludwigshafen but he refused it on the ground that it would stand in the way of his unquenchable thirst after investigations in the domain of pure science.

Fischer's views on the subject of imparting higher education in Chemistry to female students merit special consideration. He said, "Experience has taught us that the majority of the female students and even the best ones later marry and then usually are no longer able to pursue their calling. As soon as that happens the money and labour which have been spent on the study are lost and the same is true for the excessive cares which the lecturers in chemistry in the laboratory must have bestowed on their instruction."

For unveiling the secrets of nature and attainment of truth an unbiased mind is the first condition of being. And Fischer was never tired of impressing this important fact to his old students and assistants in the following terms—"*Man wird dringend gewarnt, sich bei Beobachtung der Erscheinungen, der Ausführung der Analysen und anderer Bestimmungen durch Theorien oder vorgefasste Meinungen irgendwie beeinflussen zu lassen.*"

The current of time flowed on. The first world war broke out. And Fischer had to come out from the sacred seclusion of his laboratory to help forward the cause of his country with his profound knowledge of Chemistry and experiences in furtherance of industry. As president of the numerous commissions he had to play active parts on the grave question of the supply of raw materials which were gradually diminishing. Of these, mention may be made of coal and rubber, fat constituents, ammonia, nitric acid, sulphuric acid, glycerine, oils and fats, tanning substances, and food materials for men and beasts. It was a tremendous task, and in spite of his weak health Fischer strove his utmost to cope with the situation. It was a pitiable sight when this great master could snatch a few short hours in the midst of his emergency duties to enter his vacant laboratory, as the workers had almost all gone to the front, for the solution of some modest scientific problem which proved to him as a narcotic and at the same time served as a stimulant to him.

Fischer passed away on the 15th July, 1919 leaving behind him a rich life's harvest to be reaped and enjoyed by all humanity transcending the limits of time and space.

been prepared by the action of benzotrichloride on dimethyl-
aniline in the presence of the condensing agent zinc chloride.
The lucky discoverer was Oskar Doebner (*Doebner, Ber.* 11,
1236).

In the meantime, however, the industry had prepared the
path for the bitter almond oil green. (*Emil and Otto Fischer,
Ber.* 12, 796). In the market Malachite Green was quickly
followed by the successful Victoria Green. At the same time Emil
and Otto Fischer (*E. & O. Fischer, Ber.* 12, 800, 2344) had
already explained the constitution of the rosaniline group in its
principal points. Also the green dyes which undoubtedly be-
longed to this class from the beginning soon proved identical
and received their full significance. The leuco-base in both the
compounds is the same tetramethyldiaminotriphenylmethane, and
the originally obsrved distinctions were caused by physical
isomerism. One difficulty only still lay in the explanation of
its transformation into the coloured condition. This dilema was
also finally solved by the assumption of an ammonium group
which was in chromophoric bond with the methane carbon atom
—an assumption, which was at once transferred further on to
the violet and green alkylated derivatives of Rosaniline, which
Emil and Otto Fischer obtained by insertion of the ·still missing
third amino group into the benzaldehyde residue of the green
dyestuff. In these processes of investigation neither the nitro
group, nor the ammonium group, nor even the acetyl group
showed the colour-changing action of those free primary
secondary and tertiary amino groups. Now one found why
Methyl Violet was once transformed to its green ammonium base,
the Iodine or Methyl Green, and why from this, by heating, the
tertiary violet originated again. One got to know that the
Methyl Violet (*Otto Fischer & Körner, Ber.* 16, 2904) consisted
only partly of a six-fold methylated para-rosaniline which could
not be acetylated, while another part was acetylated to a green
dyestuff or benzylated to a bluish Benzyl Violet, a proof for the
partial splitting up of the methyl group from the dimethyl aniline
in the dye-melt, which was not an ideal one. On the position
of the third amino group, however, everything depends. Only
in the para-position of the linking carbon atom its influence is

felt on the transformation from green to violet, in the meta position it shows no effect while in the ortho position the green turns into a bluish green only. Similar behaviour is shown by a hydroxyl group inserted into the benzaldehyde residue and its colour effect appears only by the addition of alkali. The reason was also disclosed for the long known colour-change from violet to green by the entrance of acids—the acids compensating the action of amino groups.

By the synthesis of para, meta and ortho-nitrobenzaldehyde green by the application of the corresponding nitrated benzoyl chloride or benzaldehyde, by condensation with salicyl and para-oxybenzaldehyde, by the reduction of their nitrated bases upto their colourless triaminotriphenylmethanederivatives, by the re-oxidation to the aminated carbinols, by acetylating or exhaustive alkylation, splitting up of acetyl or ammonium groups these fundamental statements were established by the joint investigators partly by Otto Fischer and his students in the course of a few years. Like a bright bubbling spring everything streamed forth from the first knowledge of the triphenylmethane as mother substance of the rosaniline group. Also for the rosaniline itself new ways were opened up since one had succeeded to facilitate the condensation of the primary amines (*Otto Fischer, Ber.* 12, 1693; 13, 665) by protecting the amino groups first as hydrochloric and then as sulphuric acid salts and thus to find out a new synthesis for leuco-aniline from para-nitrobenzaldehyde and aniline (*Otto Fischer & Greiff, Ber.* 13, 669). Only the smooth oxidation to the dyestuff was still missing—the nitrated aldehyde could be obtained from para-nitrobenzylchloride.

The principal results were obtained already in 1880. In that year the investigation received a new impulse.

Baeyer's Synthesis of Indigo :

As the result of a long series of systematic investigations Baeyer found (*Baeyer, Ber.* 13, 2254; *March* 1880, *D.R.P.* 11857) the most brilliant jewel in the crown of the dyestuff synthesis: the artificial preparation of the Indigo Blue from orthonitro-derivative of cinnamic acid. Of all these, the phenyl propiolic acid of Glaser, a student of Kekulé, attained after a decade the

most prospective importance. (*Glaser, Ann. d. Chem.* 1870, 154, 157). However, from the first hour onwards the inevitable side formation of para-nitrocinnamic acid at the beginning of the processes caused serious industrial consideration, because *for a successful fight with the cheap natural product the full utiliza- tion of the raw materials is necessary.* Now one succeeded to transform the para-nitrocinnamic acid into para-nitrobenzaldehyde (*Baeyer, D.R.P.* 15743 (1881); *Friedländer, Ann. d. Chem.,* •22°, 203) and with new zeal one turned to Fischer's synthesis (*Otto Fischer, D.R.P.* (1880) *No.* 16766; 1881 *No.* 16707, 16710, 16750). But the expectations were not fulfilled. The oxidation of leuco-aniline for Fuchsine still remained an insur- mountable obstacle. Only with tertiary bases and benzaldehyde, with para-nitrobenzaldehyde prepared from benzyl chloride and finally also with meta-nitrobenzaldehyde and its amino and oxy- derivatives new technical successes were achieved in the group of Acid Green, Acid Violet and Patent Blue according to the process of Acid Fuchsine (*Bad. Anil. Sodaf.* 1877, *D.R.P.* 2096 (*H. Caro*). The water-soluble basic rosaniline dyes were already obtained by the introduction of the sulpho-group to a common colouring with dyestuff acids, and then in the smooth oxidation of their leuco-sulphonic acids the appropriate method of prepara- tion was found out [*Helvetia Green, Bindschedler and Busch* 1879, *D.R.P.* 10410, *Light green S.,* 1879, *Bad. Anil. Sodaaf.* (*Fr. Kochler*); *Acid Violet* 6B. 1883, *Bad. Anil. Sodaf.* (*C. Schraube*), *Patent blue* 1888. *Höchster Farbw D.R.P.* 46384 (*A. Hermann.*]

Phosgene—a new synthetic Agent :

The synthesis of dyestuff took a new course through the introduction of phosgene into the industry. Michler's works had been published prematurely in 1876. The full significance of Fuchsine as well as the stepwise synthesis of triphenylmethane dyes were still wanting. In 1883 all this was given. There in the "Swiss country exhibition" in Zurich, in' the *Vitrine of Bind- schedler, Busch & Co.,* amazingly big crystalline violet was shown. Soon the firm at Basel joined our German industry and one got to know the origin of the product. Adolf Kern, (*Bad. Anil.*

Sodaf. 1883. *D.R.P.'No.* 27032 *A. Kern*) a former student of the Zurich Poly-technique Institute had overcome with admirable perseverance the prejudice against the industrial possibility of carbonyl chloride in an experimental manufacture, and according to the model of the old synthesis of triphenylmethane from benzhydrol and benzene, had synthesized the hexamethyl-triamino-triphenylmethane of Otto Fischer from Michler's tetramethyl-diaminobenzhydrol and dimethylaniline. Then he succeeded by smooth oxidation in converting the leuco-base to the brilliant Crystal Violet—the first 'ideal' methyl violet process. Similar results accrued from the ethylated hydrol base, from the diethyl-aniline and from a series of primary, secondary and tertiary amines of the benzene and naphthalene series. But only through the simplification of the process, according to the model of the synthesis of Aurine from phenol and dioxy-benzophenone chloride, Kern's phosgene dyes attained their industrial importance. The much more highly reactive chloride of Michler's ketone (*Bad. Anil. Sodaf.* 1883, *D.R.P. No.* 27789 *H. Caro*) condensed directly and surprisingly easily to the colour-ing compounds by the reciprocal action with tertiary bases, with diphenylamine, phenyl and tolyl naphthylamine, with phenols and even with quinoline and benzene. Out of the latter, as well as through the condensation of dimethylaniline with the chloride of the unsymmetrical dimethyl-aminobenzophenone—the benxoyl-dimethylaniline of Doebner, (*Docbner, Bcr.* 13, 2225) obtained by the degradation of Malachite Green—the green triphenylmethane dyestuff was again built up. And as the formation of the ketone itself took place in two separate stages, the method for the desired synthesis of symmetrical and unsymmetrical dyestuff derivatives of the triphenylmethane, its homologues and analogues was given in an unlimited profusion. Very soon a series of uniform violet and blue, basic as well as sulphonated dyestuffs appeared in the market, first the Crystal Violet (*Hofmann, Bcr.* 18, 767), which Hofmann had closely studied, and then Victoria Blue (*Nathansen & Müller, Bcr.* 22, 1888).

On the other hand a new family of yellow colouring com-pounds arose with primary amines through the intervention of the methane residue in the amino group—derivatives of Auramine

formed by the action of ammonia (*Bad. Anil. Sodaf.* 1884, *D.R.P. No.* 29060; *H. Caro and A. Kern*), our most ·valuable yellow basic dyes and the first representative of the Ketonimide groups (*Graebe, Ber.* 20, 3260; *Fehrmann,* 20, 2844). Through this process of development of the theoretical insight into the structure of the triphenylmethane derivatives the last questions of its homology and isomerism had naturally found a progressive solution. Hofmann's old fashion experiments with the homologues of aniline, the 'pseudo rosaniline' of Rosenstiehl and isomeric and homologous rosanilines (*Emil and Otto Fischer, Ber.* 13, 2204; *Otto Fischer and Ziegler, Ber.* 13, 671; *Rosenstiehl and Gerber, Ber.* 15, 1453, 2367; *Ber.* 17, *Ref.* 139) the reaction of homologues of dimethylaniline in the Methyl Violet processes (*Monnet, Reverdin and Noelting, Ber.* 11, 2278) and still further questions were explained till Noelting with the help of all synthetic methods (*Noelting, Ber.* 22, 2573; 24, 553) finally entered into his comprehensive "Investigations of the Dyestuff of the Triphenylmethane Group" in order to clear and supplement the richly heaped up material of observation on the legitimate effect of homology and isomerism in this field. After the conclusion of such investigations the position of each and every atom in the hundredfold dyestuff molecules of this group would be completely established in an experimental way. Then the question would be to deal with the spatial conceptions on the position of their atoms and atomic groups (*Emil and Otto Fischer, Ann. d. Chem.* 194, 290) for the physical explanation of the coloured and uncoloured conditions. In the field of known facts, as we see, there was no want of conceptions in the plane of the structural form. These assumptions of quinone-like linkings and colour conditioning atomic grouping stood in an inner relationship with the oldest conceptions of the transformation of indigo blue to indigo white, of rosaniline to leuco-aniline, of azobenzene to hydrazobenzene, above all of quinone to hydroquinone to which Graebe and Liebermann (*Graebe and Liebermann, Ber.* 1, 106) immediately after the discovery of artificial Alizarine had based their first views—"On the Relationship between molecular Constitution and Colour in organic Compounds"; theoretical representations which with the changing conceptions of the ortho

and para-quinones as double ketones, the nitrosophenols as quinoneoxide, the indophenols and indamines as derivatives of quinoneimide had already found to some extent their correspond- ing quinone-like expression in the structural forms of dyestuffs, among which rosaniline also was included [*Nietzki, Chem. Org. Farbst.* (1889), 6, 88; *Ber.* 21, 2477]. Nevertheless, in which mirror images to their chemical relation our colour changing products might appear, the connection of their molecular struc- ture with the passage of light remained a question of physics, and the solution of which would lead the theoretical dyestuff chemistry to its highest goal. (*On up-to-date researches Cf. Ostwald, Lehrbuch d. Allgem. Chem.* I, 462-473). Meanwhile the industrialist should accommodate himself to the rich treasures which appear to him as legitimate facts, but he should not dare to direct his train of thoughts to the sky-heights of science; he should remember his great ancestor *Daedalus* and should invent no waxen wings.

Also in the cause of colouring, whether the relationship of the dye-bases, acids and salts to the textile fibres rests on chemical or on physical laws, or alternately they rest on both, on this point only after further investigations of the fibre sub- stances and the fibre structure, the theory of colouring processes still in its infancy, would furnish the expected certainty. [*Knecht, Ber.* 21, 1556; *Ber.* 22, 1120; *Witt in Lehn's Farbenzeitung* 1890/91, 1; *Ostwald, l.c.* (*Adsorption*) 1079]. From the pro- cesses of development of our modern dyestuff synthesis described so far, in some instances hasty lines of thought have been pro- minent. However, it should be remembered how naturally we have proceeded from meagre conceptions to the resplendent · knowledge of our most important groups of dyestuffs, of their mother substances, families, classes, and series and thereby simultaneously from isolated discoveries to the present day constructive completion of the dyestuff fields from empirically found irrational metnods of preparation to the modern scientific transformation of the dyestuff processes. It is Kekule's theory whose circles of waves overstepping the previously fruitful fields of the simplest aromatic compounds, our intermediate products, were transmitting their irrestible momentum at once to the

structural knowledge of the oldest natural and artificial dyestuff groups. New ideas, new methods, new discoveries were added. As the torch-bearer of the new objective we see Kekule's first disciple Adolf von Baeyer and his school.

Naturally this mighty movement had gradually to draw all the other domains of dyestuffs in its orbit. A band of young investigators was ready for the operation; the models had been given, one sought for the mother substances, built up the dyes, discovered new derivatives and improved the methods of preparation. With its vast experiences and resources the industry went on helping the progress. Only some of the results of this further development we should like to consider briefly here.

Acridine Dyes :

In 1884 Chrysaniline has been recognized as diaminodiphenylacridine by Otto Fischer and Körner (*O. Fischer and Körner, Ann. d. Chem. 226, 175*). In the yellow anhydrous dyestuff base both the amino-groups occupied the para position to the methane carbon atom which links the three benzene nuclei. From the tetra-azocompound the mother substance, phenylacridine was derived in the same way as once the triphenylmethane from para-leucoaniline. By a synthesis of the dyestuff from aniline and ortho-nitrobenzaldehyde—a technical fruit of the artificial indigo-light was thrown immediately on its allied relationship to the triphenylmethane group and to its side formation in the fuchsine process, the result of a simultaneously occurring ortho-condensation; for as an intermediate product of the synthesis an ortho-diparatriaminotriphenylmethane was derived which was transformed into the diparadiaminoacridine dyestuff by oxidative fusion only. The nitrogen atom occurring in the contiguous position of the methane carbon atom of the oxidising amino-groups caused therefore here the constant ring-closure in the central group of the acridine molecule. The phenylacridine had already been obtained by Bernthsen (*Bernthsen, Ann. d. Chem. 224, 12*) from diphenylamine heated with benzonitrile, benzotrichloride and most easily with benzoic acid by using the approved condensing agent, zinc chloride, and the mother substance of the entire group, the acridine of coal-tar, the constant companion of

anthracene, came from the similar condensation of diphenylamine with formic acid. Here also the methane carbon atom effected the six membered ring closure, comparable to the memorable synthesis of the analogously constituted anthracene from ortho-benzyltoluene [*Van Dorp, Ann. d. Chem.* (1873), 169, 207], or of the anthraquinone from the ortho-benzoylbenzoic acid (*Behr & Van Dorp, Ber.* 7, 578).

Also this knowledge of constitution of the oldest yellow aniline dyestuff had to manifest its industrial effect sooner or later. First one improved the separation of the important Chrysaniline or " Phosphine ", much valued because of its fastness and applicability as mixed dye, mainly with Safranine, then one found by the condensation of benzaldehyde with meta-toluylenediamine a process for the preparation of Benzoflavine (*K. Oehler,* 1887, *D.R.P. No.* 43814 *C. Rudolph*), a diamino-dimethyl-phenylacridine homologous and isomeric with Chrysaniline. The ring-closure occurred here by the splitting up of an amino group, finally, the so formed hydroacridine base was oxidized. Benzaldehyde was followed by its nitrated and aminated derivatives and in 1889 by formaldehyde—the course being the same as in the synthesis of the triphenylmethane group [*A. Leonhardt & Co.* 1889. *D.R.P. No.* 52324 (*F. Bender*)]. A series of valuable yellow and orange red acridine dyes were obtained and for the synthesis of one such " Acridine Orange " metaaminodimethylaniline was used.

By oxidising acridine a dicarboxylic acid of quinoline is obtained and quinoline itself is again the mother substance of a group of dyestuffs (*Graebe and Caro, Ber.* 13, 99). Also here we come across the already well-known synthesis.

Quinoline Dyes :

According to the model of the process of Malachite Green Emil Jacobson (*Jacobson, D.R.P. No.* 19306, 23188; *Jacobson and Reimer, Ber.,* 16, 513, 1082, 2602) heated the coal-tar quinoline with benzotrichloride and obtained a red fluorescent dyestuff, by the introduction of bromine the colour-tone of which was raised to violet. Benzalchloride shows a similar reaction, and with phthalic anhydride yellow coloured condensation pro-

ducts are formed. Related phenomena are disclosed in the pyridine series and in the homologues and analogues of quinoline. But it was soon recognized—as once in Aniline Red—that it was not the pure quinoline formed by Skraup's synthesis was the source of the dyestuffs, Quinoline Red and Quinoline Yellow. Here also the methyl groups of the homologous bases have influenced the formation of coloured molecules. However, the analogy does not go further with the synthesis in the triphenyl-methane group. The yellow dye-stuff, prized for its picric acid-like colour tone, the " Quinophthalene "—its water-soluble sulpho acid being used—is formed, without any assistance of quinoline, by the condensation of equal molecules of homologous synthetic quinaldine and phthalic anhydride. For Quinoline Red, Hofmann however proved in his last brilliant dyestuff investigations (*Hofmann, Ber.* 20, 4; *Act. Ges.f. Anilf. D.R.P.* 1886 *No.* 40420) that it can be produced in considerable quantity only from the isomeric companion of quinoline, the isoquinoline mixed with quinaldine [*Hoogenwerff and Van Dorp, Ber.* 18, 384C; (*Cyanine*) *Ber.* 18, 75C]. The structure of these dyestuffs has not yet been conclusively proved.

The light sensitiveness of the brilliantly coloured Quinoline Red prevented its lasting entrance into the dyeing industry as had once been the case with the oldest dyestuff of this group, the Quinoline Blue or Cyanine, but owing to their unfastness they proved to be excellent sensitizer for the demand of the art of photography which in the meantime had attained scientific development by the investigations of Vogel, Eder and others. Guided by the characteristic absorption spectra of the dyestuff groups, probably also by the supposition on the relation of light absorption and light stability, one tried to dye the photographic plates with coal-tar dyes, first with Coralline (*H. Vogel, Ber.* 6, 1302; 17, 1196; *D.R.P.* 39779), Aldehyde Green and Magdala Red, then chiefly with Eosine, thereby increasing in a surprising manner its light-sensitiveness against those yellow, green and red rays which were otherwise not or little active and finally attained by suitable choice of the dyestuffs and by corresponding improvements in the preparation of such " orthochromatic ". brom-silver-gelatine plates, the photographic reproduction of the

spectra and of all coloured objects in the correct proportions of brightness, in which their colours appear to our eyes (*Eder, Wiener Monatsch f. Chem.* 1886, 22). And not only to the scientific investigation on the colour of ions and to the art the new reagents became useful in this way, but the industrialist also now began to examine the photography of the spectrum for the finest distinctions between the members of the dyestuff series prepared by him.

Anthraquinolines :

The transition from quinoline to the anthracene group is formed by the anthraquinoline, the previously mentioned mother substance of the Alizarine Blue and its hydroxyl-rich green and bluish green derivatives; with the rosaniline group they are connected by the Aldehyde Green, the constitution of which had already been known. According to the investigations of Wilhelm *v.* Miller and Plöchl (*Ber.* 24, 1700; *Ber.* 22, 227) the dyestuff obtained from Lauth's Aldehyde Blue with hyposulphite is a fuchsine derivative, in which the methane carbon atom is linking up a quinaldine residue with two aniline aldol residues, which themselves again are connected by a sulphur atom. The Aldehyde Blue is still exclusively an aldol derivative, comparable to the alkylated violets. In this case the transition from blue to green is caused by the then occurring quinoline formation. Also the previous synthesis of Quinoline Green, from the chloride of tetramethyldiamino-benzophenone and quinoline, differentiated from that of the Crystal Violet through the exchange of dimethyl-aniline against the tinctorially indifferent quinoline. Only with the hydrogenation of quinoline in the pyridine ring its colour-producing functions awake again. For, the comprehensive hydrogenation studies of Eugen Bamberger are probably going to meet a technical future (*Bamberger, Ann. d. Chem.* 257, 21, 28). We know from his work that quinoline by the conversion into the tetrahydro-derivative assumes the properties of a nitrogenalkylated aniline and in numerous dyestuffs-formations this student of Baeyer has proved " that all tetrahydroquinolines are genuine nitrogen-alkylated anilines, whose alkyl possesses the generally unessential property of the ring-forming atomic order ":

significant points of view for the later dyestuff investigation. Accordingly Fischer's syntheses in the triphenylmethane group were transferred to the quinoline group, and out of tetrahydro-quinaldine violet and green dyestuffs came forth. (*V. Miller and Plöchl, Ber.* 24, 1715).

Indole Group :

From quinoline we reach indole, which is poorer in carbon and is the mother substance of the indigo group. On the way we come across many reciprocal actions in the history of development of the mother substances and their groups of dyes. Already in 1879 we have seen the formataion of quinoline from allyl-aniline (*Königs, Ber.* 12, 453) and two years earlier indole had been derived from ethylaniline and its homologues by a similar pyrogenic reaction (*Baeyer and. Caro, Ber.* 10, 692, 1262). In 1869 the oldest indole synthesis was effected through the reducing potash fusion of orthonitrocinnamic acid (*Baeyer and Emmerling, Ber.* 2, 679), its immediately following counterpart was the first formation of Indigo in traces from orthonitroacetophenone (*Emmerling and Engler ; Ber.* 3, 885; *Engler, Ber.* 18, 2238). However, shortly before Baeyer (*Ber.* 3, 514) had reduced isatin to Indigo Blue and when in 1878, the year of the synthesis of triphenlymethane, he again entered his indigo synthesis, conducted according to definite plan (*Baeyer, Ber.* 11, 582, 1228, 1296; *Ber.* 12, 456, 1309; *Ber.* 13, 2254) and when he obtained in a chain of smooth running operations from the orthoamino-phenylacetic acid its inner anhydride: the oxindole, from the nitroso-oxindole isatin, from isatinchloride Indigo Blue then only the oldest indole and indigo syntheses attained their recent momentous significance. The first synthesis of artificial Indigo in spring 1880 from orthonitrocinnamic acid was followed by the aldol condensation of orthonitrobenzaldehyde with acetaldehyde or acetone (*Bad. Anil. Sodaf. D.R.P.* 1882 *No.* 19768; *Baeyer and Drewsen, Ber.* 15, 2856) and then followed the synthésis of the dyestuff from orthonitro and orthoaminoacetophenone brominated in the side chain (*Bad. Anil. Sodaf. D.R.P.* 1882 *No.* 21592, 1883 *No.* 23785; *Baeyer and Bloem, Ber.* 17, 963). And while in all directions and with almost unexampled perse-

verance the new ways to Indigo Blue were investigated in all laboratories and workshops the reflex of these investigations was noticed always in the neighbouring domain of the quinoline. Already the formation of Indigo from isatin chloride had led Baeyer (*Baeyer, Ber.* 12, 456, 1320) to a similar synthesis of the quinoline from hydrocarbostyril and as soon as the ortho-nitrocinnamic acid ester had become a commercial product, carbostyril prepared, from it was proved to be ∝oxyquinoline (*Friedländer. and Weinberg, Ber.* 15, 2103). Also from the condensation of the then available orthoaminobenzaldehyde (*Friedländer and Goehring, Ber.* 16, 1833) with acetaldehyde or acetone, quinoline or quinaldine was obtained. In a similar way (*O. Fischer, Ber.* 19, 1036) ∝γ-dimethylquinoline was derived from orthoamino-acetophenone and acetone as well as the corresponding phenylmethylquiholine or ∝-Phenyl-γ-lepidine, from orthoaminoacetophenone and acetophenone. So the structure of quinoline and its derivatives, particularly for the synthesis of artificial healing agents was cleared up; the phenyl lepidine however proved to be at the same time the " flavoline " as well as it furnished the previously obtained mother substance of the Flavaniline by the degradation of its para-amino group. By a fairly similar synthesis of ortho with para-amino-acetophenone the fluorescing yellow dyestuff was again built up, which the industry had discovered in 1887 (*Höchster Farbwerke, D.R.P.* 1881. *No.* 19766; *Ch. Rudolph and O. Fischer, Ber.* 15, 1500) through " Hofmann's atom-wandering " by heating acetanilide with zinc chloride and had brought to a short lasting application.

After several years the reminiscences of the oldest indole and indigo syntheses in the potash fusion, of the aminophenylacetic acid of oxindole, of the aminoacetophenone of Indigo and quinoline, of the acetanilide of Flavanilines were newly awakened. Again one went back to the beginning, but the light of investigations of Baeyer and his school illuminated the paths!

Indigo :

Already in 1883 Baeyer had completed (*Baeyer, Ber.* 14, 1741; *Ber.* 15, 50, 775; *Ber.* 16, 2188) his investigations " On the Compounds of the Indigo Group" in their principal outlines

and the constitution as well as the conditions of formation of
this wonderful group were established on an experimental way.
In its structural form appeared the Indigo Blue—corresponding
to its synthesis from diphenyldiacetylene and diisatogen—as a
symmetrical combination of two carbonyl and imide containing
" indogene groups ", effected by the combination of indoxyl and
isatin in their labile or " pseudo " forms; the oxygen-free mother
substance of each of the indogene groups is the indole.

Recently in the light of this knowledge, almost simultane-
ously from diverse quarters, a new turning point was reached
in the synthesis of Indigo, and this infused also a new life to
the sunken hopes for the reduction of cost price of the artificial
dyestuff.   In the meantime one had indeed accomplished the
synthesis in the isatin group (*Elberfelder Farbenfabriken. D.R.P.
1883 No. 25136, 27979; P. Meyer, Ber.* 16, 924, 2261 ; *Duisberg,
Ber.* 18, 190) by the action of dichloroacetic acid on aniline and
its homologues, mainly on paratoluidine and now one also strove
towards the formation of pseudoindoxyl from aniline and mono-
chloracetic acid.   The surprising novelty—though also technically
difficult, was the old potash fusion.   The ring-closure of the
molecule was followed here by its explosion in no time; indeed
once the potash fusion of Indigo, the Arabian *Anil* bestowed on
the oil coming forth from it the name aniline !

The impulse to the new movement was given in 1890 by a
communication from Flimm (*Ber.* 23, 57) in the first issue of
the " Berichte ".   In the potash fusion of the monobromacetani-
lide arose a new colourless compound, which immediately by the
admission of air was transformed into the blue dyestuff, pro-
bably the much sought for pseudoindoxyl.   But the formation
of Indigo was scanty.   Then for the first time Karl Heumann
(*Heumann, Ber.* 23, 3043, 3431 ; 24, 977; *D.R.P. 5th May* 1890,
No. 54626, *Bad. Anil. Sodaf.*) of the Technical High School in
Zurich applied " the groups of atoms in the required sequence ",
grasped at the phenylaminoacetic acid, the phenylglycocoll, which
can be easily prepared from aniline and monochloracetic acid, and
obtained by the potash fusion the indigo producing substance.
Similar and partly even more encouraging results were attained
by substituting phenylglycocoll with its homologues and deriva-

tives.   Anthranilic acid which had been obtained about the same
time according to Hofmann's beautiful method of oxidation of
the acid amide, the phthalimide, specially suited in this respect
(*Hofmann, Ber.* 14, 2725; *Bad. Anil. Sodaf., D.R.P.* 1890
No. 55988) and the cheap naphthalene now promised to become
a good source of the dyestuff.   So with new zeal the industry
turned to the solution of its big task and found at once that the
ring-closure in the molecule can also be completed by means of
sulphuric acid anhydride (*Heymann, Ber.* 24, 1471; *Knietsch,
Ber.* 24, 2086) but with a simultaneous sulphonation occurring.
Again patent upon patent followed.   However, technical success
was not reported in the market.   For difficult is the beginning
of the struggle against the natural product with its lowered price:
but even then the possible improvement and extension of the
plantation of the indigo plants still wildly growing on extensive
stretches of the earth's surface and the rational extraction of the
commercial product rich in dyestuff would not mean a war of
extermination in the near future as it had been the case with
the madder roots.   However chemistry finally won, though
probably through other and better products only!

Aniline-Dyes :

So Indigo leads us back again to the province of the Aniline
dyes.   Here one had found an abundance of dyestuff reactions
from the earliest times of the oxidation experiments with amines
and phenols, whose knowledge bestowed on the industrialists the
certainty of the path-finders and in some cases also led him to
scientific diagnosis.   This treasure of experience increased daily.
However, let us recapitulate here a few well known facts only.
It was found that in Runge's calcium chloride reaction with
aniline admixed with phenol a dyestuff like litmus was formed
(*Bechamp, Rep. Chim. Appl.* 1861, 130), and phenol containing
ammonia showed a similar reaction (*Berthelot, Rep. Chim. Appl.*).
Also with nitrous acid and excess of phenol [*Lex. Ber.* 3, 457;
Meer : Ber. 8, 625 *from nitrosophenol ; Hirsch, Ber.* 13, 1909 ;
from chloroquinoneimide] was obtained by alkaline reduction a
vat dye which turned deep blue in the air.   By the action of
sulphuric acid containing nitrous acid on phenol. Liebermann had

obtained (*Liebermann, Ber.* 7, 247, 1098) in 1874 a series of stable dyestuffs, including the brilliantly fluorescing Weselsky's diazoresorufin (*Weselsky* 1872, *Ann. d. Chem.* 162, 273). And as shortly afterwards by heating nitrosodimethyl aniline hydrochloride with phenol, or by the addition of sulphuric acid to a solution of nitrosophenol in phenol, the formation of the same or similar vat dyes was observed, Baeyer proclaimed (*Baeyer and Caro, Ber.* 7, 966) Liebermann's reaction as a reaction on the then newly introduced nitroso-group, firstly effecting the diphenylamine-like combination of similar molecules of the paranitroso compound, and of the phenol to a colourless compound, which then by oxidation or further condensation furnished the dyestuff. Weselsky's diazoresorcin is formed apparently in a similar way from nitrosoresorcin and resorcin. Further it was shown, that ·by boiling with caustic •soda the nitroso base was transformed into nitrosophenol and that by reduction the corresponding paraamino-compounds were formed.

However, one had met with the paradiamines already in the mother liquor of the oldest Induline and Safranine-melts of aminoazo-compounds with aniline or toluidine. Oxidising agents at once caused an intense green or blue colouration in the lyes and by further addition quinone originated as Hofmann had found out at first in his discovery of the paradiamines. In the naphthalene series also by the oxidation of the naphthalene diamine, obtained from aminoazonaphthalene ·by the splitting of the tin-salt, the characteristic green colouration had been observed by Perkin in 1866 (*Perkin, Ann. d. Chem.* 137, 365). This was generally held to be a dyestuff reaction of the pure paradiamine (*Witt, Ber.* 10, 874). Nevertheless, this was an illusion as once it had been with the formation of Aniline Red from the supposed pure aniline. In 1877 Hofmann's student Robert Nietzki first proved soon after the commencement of his successful investigations (*Nietzki, Ber.* 9, 1168; 11, 1093; *Ann. d. Chem.* 215, 125), which led him after the first investigations of Aniline Black to the field of quinone and hydroquinone—that only pure paratoluylenediamine in conjunction with orthotoluidine can be oxidized to the green dyestuff; a process, which in the then usual way was explained by him by the co-operation of the methyl

group, according to the analogy of the formation of Rosaniline (*Nietzki, Ber.* 10, 1157). Weber had however reported shortly before that pure paraaminodimethylaniline gives only a brilliant red colouration by oxidation (*Weber, Ber.* 10, 762).

On the extraordinary reactivity of this red compound (*Bad. Anil. Sodaf.* 1877, *D.R.P. No.* 1886, *H. Caro ; Friedländer, Fortschr. der Teerfarbenf. I,* 248; *Würster, Ber.* 12, 530, 1803, 2071) which is formed from para-aminodimethylaniline as well as from nitrosodimethylaniline in the initial stages of their corresponding oxidation or reduction, the processes for the preparation of Methylene Blue from nitrosodimethylaniline discovered in 1876 and para-aminodimethylaniline obtained therefrom as well as by the reducing fusion of the dimethylated aminoazocompounds were depending. Methylene Blue is obtained if hydrogen sulphide is passed through the " strong acid solution of the colourless, unstable oxidation product " immediately after its formation.

In these processes following one another in rapid succession lie the character of the apparently simultaneous oxidation of paradiamine and hydrogen sulphide in Lauth's reaction (*Lauth, Ber.* 9, 1035) and on the action of such reactive intermediate products—which are now conceived to be as analogues to the quinone chlorimide (*Schmitt and Bennewitz. Jahres Ber.* 1873, 726; *Hirsch, Ber.* 13, 1903) and quinone dichlordimide (*Krause, Ber.* 12, 47) the formation of those partly fugitive, partly unstable green, blue, violet and red dyestuffs depended. These observations, as already mentioned, go back to the oldest times of the aniline dye industry, back to Perkin's Violet and Safranine and further still to Runge's calcium chloride reaction. This complicated field of the colour phenomena has been elucidated by investigation during the last decade and has been opened for systematic research.

Now one knows, that those green and blue compounds through acids easily decompose and quinone forming Indamines and Indophenols come forth from the apparently simultaneous oxidation of one molecule of a paradiamine or para-aminophenol and one amine or phenol with free para-position. In a similar smooth manner react nitrosodimethylaniline and its analogues as

well as the quinone oxime and quinone chlorimide. Compounds of this type from benzene, naphthalene, pyridine and quinoline series are known (*Lellmann, D.R.P.* 46938; *Ber.* 21, 287; *Bamberger, Ann. d. Chem.* 257, 28). Huge is the number of their substitution derivatives already represented. The first was Toluylene Blue, an aminated indamine, investigated in 1879 by Otto Witt and derived from nitrosodimethylaniline and meta-toluylenediamine (*Witt, Ber.* 12, 930). The first and the only practically used indigo substitute Indophenol was obtained from nitroso or para-aminodimethylaniline and ∝-naphthol by the same investigator jointly with the great colourist Horace Koechlin in 1881 (*Koechlin and Witt, D.R.P.* 1881 *No.* 15915; *Witt, J. Soc. Chem. Ind.* 1882, 255). Even on the fibre the smooth formation of the beautiful sufficiently light- and wash-fast dye-stuff could be obtained. Nevertheless its sensitiveness to acid has prevented its extensive use. Now one also came to know the mother substance from which the acid-fast leuco-compounds of indamine and indophenol are formed by the entrance of amino and hydroxyl groups. These are according to the fundamental investigations of Nietzki and in agreement with Baeyer's previous explanation of the " nitroso reaction ", diphenylamine, its homologues and analogues (*Nietzki, Ber.* 16, 472; *Bindschedler, Ber.* 16, 864; *Mohlau, Ber.* 16, 2343; *Witt, Ber.* 17, 76). The simplest leucoindamine is Nietzki's paradiaminodiphenylamine. The transition into the coloured condition is here also analogous to that of hydroquinone into quinone. From the ring-forming imino group and from an amino group an atom of hydrogen is eliminated and the atom-grouping of the hypothetical quinone-diimide is formed. Similarly the indophenols can be taken as derivatives of quinoneimide. And as nitroso dimethylaniline is . easily transformed into nitrosophenol, so indamines derived therefrom change progressively into the indophenols by heating with alkali.

Safranines :

This theoretical knowledge was the fruit of technical investigations on the process of formation of Safranine. With its characteristic instinct the dyestuff practice had discouraged a

rational process first in Switzerland from the beginning of the 7th decade. As previously, one prepared from the toluidine-rich *Echappés** of fuchsine manufacture, a mixture of aminoazo-compounds with excess of monoamine. This however was heated no more with oxidising agents or acids but it was decomposed previously by zinc dust reduction and the mixture of monoamine and paradiamine thus obtained was oxidized. On heating the initial blue colour gradually changed to luminous Safranine Red. This striking transformation was noticed even in the cold. The process consisted therefore, as even now, in the action of primary amines on the Indamine formed in the first phase of the re-action. With the publication of this technical improvement, which was immediately strongly felt through the falling market price of Safranine, the industrialists were forced to experiment in the new direction. Prospects opened on ever increasing com-binations of paradiamines and amines. Everything was thoroughly investigated, the conditions of formation of the Indamines and Safranines were ascertained, the number and nature of the molecules entering into reaction were fixed. It was found that the conversion of the blue into the rd dyestuffs occurred only through primary amines and also through those with occupied para-position, while some orthosubstituted monoamines proved to be ineffective (*Nietzki, Ber.* 19, 3163). One discovered actual or apparent isomerisms (*Nietzki, Ber.* 16, 471 *and Schweitzer, Ber.* 19, 150), built up symmetrical and unsymmetrical Safranines, from the " Phenosafranine " out of paraphenylene diamine and pure aniline up to the complicated combinations. Yet only a few approved commercial products emerged from these voluminous experiments. Greater was the scientific gain. Bindschedler (*Ber.* 13, 207; 16, 867), Witt (*J. Soc. Chem. Ind.* 1882, 255), Nietzki (*Ber.* 16, 464) and Andresen (*Ber.* 19, 2212) published their experiences gained through practice and widened the foundation for the knowledge of this group of dyestuffs which had originally been laid down by Hofmann and Geyger in 1872 (*Hofmann and Geyger, Ber.* 5, 526).

Only in 1883 Nietzki's researches cleared the path to a

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* Aniline rich in o-toluidine which distils over during the manufacture of Magenta (Aniline Oil for Safranine).

constitutional knowledge of the Safranines. Previously attempts had been made for the interpretations of the empirical formula only as it had once been in the case of Rosaniline. Now Nietzki based his investigations mainly on a careful investigation of Phenosafranine, which he built up synthetically from equal molecules of paradiamino-diphenylamine and pure aniline. He found that the dyestuff contained besides both the amino groups standing in the para-position to the linking nitrogen atom which served for the synthesis of indamine still "a very strong basic group analogous to the ammonium group" and which could neither be acetylated nor diazotized. However the theoretical views were still under the then over-riding influence of the grand achievement in the triphenylmethane domain. Nietzki's formula for the " most simple Safranine " resembled that of the " simplest Rosaniline ", as the mother substance of the leuco-bases appeared to be the triphenylamine, the leucophenosafranine is like the para leucoaniline, a triamino-derivative. From many points of view this formula seemed to be much better than its speculative fore-runners, particularly from the formation and behaviour of the safranine group but it did not explain the colour-tone, the characteristic fluorescence, and above all the great stability of the safranines in comparison to the intermediate products, the Indamines. But the fields of other dyestuffs had not yet come into the picture.

Methylene Blue :

At the same time August Bernthsen, a student of Kekulé entered into his comprehensive investigations of the acridine and methylene blue groups. Soon he had cleared up the long con-tested structure of the sulphur containing dyestuff and its numerous related compounds (*Koch, Ber*, 12, 592, 2069; *Mohlau, Ber*. 2728; *Ber*. 17, 102; *Erlenmeyer, Ber*. 16, 2857). Nietzki's and Bindschedler's explanations served as a clue to the modes of formation and constitution of the indamines. Starting from a correct analysis of the Methylene Blue and its leuco-compound which now gave only three nitrogen atoms instead of four, found previously by others, Bernthsen at once supposed a diphenylamine like combination of 2 moleclues of the paraaminodimethylaniline

and went on to the confirmatory synthetical experiment
(*Bernthsen, Ber.* 16, 1025, 2896; *Ber.* 17, 611; *Ann. d. Chem.*
(1885), 230, 73). By heating diphenylamine with sulphur he
obtained thiodiphenylamine and proved that the sulphur atom
had entered into both the benzene nuclei. Then he built up the
dye molecule by nitrating and aminating. A leuco-base was
formed which was easily oxidized into a violet dyestuff. This is
identical with Lauth's Violet from paraphenylenediamine and the
Methylene Blue is 'its tetramethylated derivative while deriva-
tives analogous to indophenol are produced by heating with
alkali. Thus the thiodiphenylamine proved to be the mother
substance of the leuco-compounds in the Methylene Blue group.
The transition into the coloured and colouring condition was
completed here in the same quinone-imide-like manner as with
the indamines and indophenols from which the dyestuffs are
derived by the introduction of the sulphur atom. But this in-
troduction does not occur into the finished indamines—so obvious
also from Bernthsen's first communications—their " fixation "
being considered to have taken place through sulphur. Never-
theless the ceaselessly experimenting industry solved this insolu-
ble problem in 1885 (*Höchster Farbwerke D.R.P.* 1885, *No.*
38573 *E. Ulrich*). Out of a joint oxidation of para-amino-
dimethylaniline and dimethylaniline in the presence of sodium
hyposulphite and zinc chloride Methylene Blue emerged! How-
ever this was only an apparent and incomplete solution of the
problem. At first the entrance of the hyposulphurous acid resulted
only in the red quinonediimide-like oxidation product of the
paradiamine, a thiosulphonic acid of the aminodimethylaniline
being smoothly formed and then only in the second phase of the
reaction, the Indamine was obtained. By the subsequent heating
of the zinc chloride and chromic acid containing mixture, the
linking of both the benzene nuclei was completed through the
sulphur atom. In a similar way by substituting the para-amino-
dimethyl aniline and dimethylaniline by other paradiamines and
amines or phenols symmetrical and unsymmetrical, homologous
and analogous members of the Methylene Blue group were
obtained.

The nature and rational manipulation of this elegant and
technically successful synthesis was disclosed first by Bernthsen

jointly with the industry and in the further course of his memorable investigations (*Bad. Anil. Sodaf.* 1887 *D.R.P. No.* 45839, 1888, *No.* 47374; *Höchster Farbwerke,* 1888, *No.* 46805, 47345; *Bernthsen, Ann. d. Chem.* 1888, 251, 1). It was the fruit of his discovery of the Methylene Red, a by-product in the manufacture of Methylene Blue, during the formation of which the sulphur atom had entered into the paradiamine molecule only. On reduction it furnished the paradimethylamino-derivative of the orthoaminophenyl mercaptan discovered by Hofmann (*Hofmann, Ber.* 12, 2359; *Ber.* 13, 8, 1223). Through alkali besides the corresponding disulphide, a Methylene Red regenerating "supersulphide" and that "thiosulphonic acid" capable of being synthetically produced with sodium hyposulphite, were formed. Through chemical transformations these sulphur containing compounds were related to each other. The mercaptan and the disulphide proved to be components of Indamine and Methylene Blue. Although Methylene Blue remained as before technically the most important dyestuff of the group, the progress of the industry had nevertheless been greatly enhanced by its improved method of manufacture. However, the broadening of the scientific outlook must manifest its influence on other fields of dyestuffs.

Scarcely had the anthracene and acridine-like structure of thiodiphenylamine been recognized, scarcely had the almost simultaneously discovered synthesis of Chrysaniline and of Lauth's Violet been made public when it was supposed that the dyestuff molecules of the safranine group owe their fastness to an analogous six membered ring closure. The orientation of the chemistry of that time favoured such ideas. Also in other synthetic fields an unexpectedly rich world of ring-forming structures had then been disclosed! So almost innumerable syntheses in the quinoline and indole groups followed, among others, the pyridine-like compounds of Hantzsch, the quinazoles of Emil Fischer, the pyrrole and pyrazole derivatives of Knorr, the thiophene of Victor Meyer and quinoxaline of Hinsberg. The first experimental proof of the existence of a ring-forming combining group in safranine-like dyestuffs was furnished by Witt with the discovery of the Eurhodines.

Eurhodine :

From the orthoaminoazotoluene, long sought for in vain, (*Noelting and Witt, Ber.* 17, 77), Witt obtained in 1885 by melting together with ₐ -naphthylamine hydrochloride, the first representative of a supposed new class of dyestuff whose properties at the same time reminded one of those of the Safranine and Chrysaniline. These dyestuffs which can be prepared from all orthoaminoazocompounds, share with the anthraquinone derivatives the capacity to sublime. And as the corresponding Chrysophenol is formed from Chrysaniline by heating with hydrochloric acid the phenol-like Eurhodol, though still retaining basic properties, is formed from Eurhodine. By eliminating the amino group according to the method of Griess, Witt now tried at the beginning of 1886 to prepare the mother substance of Eurhodine. The compound thus obtained reminds strongly of the β -naphthylene-toluquinoxaline produced meanwhile from β -naphthaquinone and orthotoluylenediamine by Hinsberg (*Hinsberg, Ber.* 18, 1229; *Ann. d. Chem.* 237, 327). In this compound a six membered ring symmetrically closed by two nitrogen atoms forms the linking of the toluene and naphthalene molecules. From phenanthraquinone and para-amino-orthophenylenediamine formed from 'Chrysoidine by fission through reduction as Eurhodine of undoubted quinoxaline structure was again built up.

Discoveries after discoveries followed in quick succession. Witt's attention was drawn to the Toluylene Red, known in commerce as Neutral Red and it was prepared by him in 1879 by heating his Toluylene Blue (*Witt, Ber.* 12, 937; *D.R.P.* 1880 *No.* 15272, *Cassella & Co.*). Unmistakably these Eurhodine and Safranine-like dyestuffs were derived from an Indamine, the linking nitrogen, atom of which is orthoaminated and from his renewed investigations a further insight into the constitution of both the groups of dyestuffs was expected. In agreement with Witt Bernthsen made the decisive experiment.

Phenazine :

Shortly before Merz had obtained Methylphenazine by the condensation of orthotoluylenediamine with catechol which was claimed to be the next higher homologue of diphenyleneazine or

Phenazine analogously constituted to anthracene and acridine (*Merz, Ber.* 19, 725; *Ris, Ber.* 19, 2206; *Claus, Ber.* 5, 367). Here both the methene groups of anthracene were fully replaced by nitrogen atoms. Soon Phenazine itself also resulted from the same condensation of orthophenylenediamine and catechol and it was proved to be identical with the old azophenylene of Claus and Rasenack.

In the mean time Bernthsen (*Ber.* 19. 2604) had already come to the conclusion that Phenazine was the mother substance of the dyestuff of the Toluylene Red group. By the combined oxidation of equal molecules of paraphenylenediamine and meta-toluylenediamine he prepared the " most simple Toluylene Blue " and from that the " simplest Toluylene Red." Then he eliminated the diazotizable amino groups and Merz's Methylphenazine came into being. The Toluylene Red of Witt is therefore dimethyldiamino-methylphenazine and the dimethylaminomethylphenazine obtained through the degradation of its primary aminogroup was at once proved to be Eurhodine. The transition of the blue aminated Indamine into the stable red fluorescing Phenazine derivative depended consequently on an " orthocondensation ", as the previously mentioned conversion of the orthodiparatriamino-triphenylmethane into the diaminophenyl-acridine, the Chrysaniline.

The apparent relationship of Toluylene Red and Safranine forced at once to the assumption that in both the azine grouping was present as a common family bond. Just as it arises in Toluylene Red from the diphenylamine nitrogen and the nitrogen atom of the amino group, which in Toluylene Blue is fixed already in the orthoposition, so it should be formed in a similar way from the amino-group of the newly entered primary mono-amine by the conversion of Indamine into the phenyl-rich Safranine. Its nitrogen atom had to be linked to both the benzene rings already linked together, and this ring-closure was to bestow the Methylene Blue-like stability on the Indamine molecule. However, if the blue Indamine derived from quinone be converted into a true Phenazine derivative, then also both the ring-nitrogen atoms must enter into an alliance linking with one another. This involves the further assumption that the formation

of Safranine under the disruption of the quinonediimide grouping of Indamine depends on the formation of a peculiar phenyl-azonium group. This would explain the strong basic character of the oxygen-containing safranine base and also many other of its properties.

Bernthsen was the first to suppose (*Bernthsen, Ber.* 19, 2690) that the Phenosafranine " is a true Phenazine derivative, a diaminophenylphenazonium chloride." In the formula assigned by him both the amino groups appear in symmetrical position to each of the ring-nitrogen atoms. Almost simultaneously Andresen attained (*Andresen, Ber.* 19, 2212) a similarly symmetrical indamine formula of Phenosafranine by comparative considerations on Methylene Blue and Safranine. Witt however soon showed (*Witt, Ber.* 19, 3121) that only an unsymmetrical formula would satisfy the observed cases of isomerism in the preparation of alkylated Safranines as well as the true mechanism of reaction. In his structural formula of the Phenosafranine the thought was expressed that the nitrogen and the nucleus of the reacting aniline participate in the reaction which is identical with the case of the reacting Indamine. The nitrogen atom of aniline attached itself to a benzene nucleus of the Indamine, the linking nitrogen of Indamine does the same with the benzene nucleus of the aniline and the phenazonium group is built up on the original diphenylamine nitrogen. This view was supported by Nietzki (*Nietzki, Ber.* 19, 3163), who adduced new proofs for the isomerism of the alkylated safranines and the inability of the diorthosubstituted primary amines for the conversion of diamino-diphenylamine into Safranine. Soon afterwards Witt gave a synthetical proof for the existence of similar azonium bases by the preparation of such a dyestuff from phenanthra-quinone and phenylorthonaphthylenediamine (*Witt, Ber.* 20, 1183). But neither the degradation of Phenosafranine to its mother substance was successful nor were other constitutional questions in this field conclusively solved (*Nietzki and Otto, Ber.* 21, 1598). Nevertheless, much has been attained through theo-retical investigations. In progressive factories uniform Safra-nines were manufactured and the knowledge that normally reacting diazo-compounds derived from one of their amino groups whose azodyestuff-combination with the naphthols still preserve

the strong basic and salt-forming character of the azine dyestuffs
has led lately to the industrial utilization of the valuable deep
blue coloured Indoine (*Bad. Anil. Sodaf. D.R.P.* 1891, *No.* 61692
P. Julius).

The insight into the nature of the Safranines gained up to
the end of 1886 was followed by the knowledge acquired in the
same year in Nietzki's laboratory of Naphthalene or Magdala Red
as a Safranine dyestuff of the naphthalene series which Hofmann
had first investigated in 1869 (*Julius, Ber.* 19, 1365). And soon
the first light also fell on the constitution of that still mysterious
Perkin's Violet, which Hofmann had already supposed to be a
phenylderivative of the Safranine (*Hofmann and Geyger, Ber.* 5,
532).   In conjunction with a friend from the industry Otto
Fischer prepared a phenylated Safranine which was proved to be
identical with the simple pseudomauvein described by Perkin
[*Otto Fischer and Edward Hepp* (*Kalle & Co.*) *Ber.* 21, 2620;
Höchster Farbwerke D.R.P. 1888 *No.* 49853].   It was produced
from Witt's nitrosamine which both had obtained in common
through rearrangement by means of alcoholic hydrochloric acid
of nitrosodiphenylamine on aniline hydrochloride (*Witt, Ber.* 8,
855; *Fischer and Hepp, Ber.* 19, 2994).   As usual in Safranine-
melts of that kind, the closely related Indulines resulted at the
same time.   This discovery was made at the beginning of the
" Studies in the Induline Group ", which both the investigators
accomplished with brilliant success (*O. Fischer and Ed. Hepp,
Anh. d. Chem.* 256, 233; 262, 237; 266, 249).   In their investi-
gations of several years and beset with difficulties the progressive
reciprocal action of theory and practice was again clearly dis-
closed and the personal intercourse of their representatives was
also manifest.

Indulines :

Before the beginning of those investigations deep darkness
prevailed on the wide field of Indulines (*Fischer and Hepp, Ber.*
20, 1253, 2479).   The fast dyes of this group had attained an
ever increasing industrial significance. One improved the original
process described by Hofmann and Geyger (*Hofmann* and *Geyger,
Ber.* 5, 472), by v. Dechend and Wichelhaus (*Ber.* 8, 1609), by

Witt and Thomas (*Ber.* 16, 1102; *D.R.P.* 1881, *No.* 17340);
prepared spirit and water soluble Indulines, Fast Blues and
Nigrosines in all forms of shades; enabled the insoluble dye-
stuff for the calico printing by the application of suitable solvents,
first of the tartaric acid ethyl ester and finally of the harmless
and active "Acetine" (*Bad. Anil. Sodaf. D.R.P.* 1886,
No. 37064, *C. Schraube*)—or one produced tannin-mordant
dyeing. water soluble, aminated Indulines (*Dahl & Co. D.R.P.*
1886 *No.* 36899) through dyemelts with paraphenylene diamine.
With renewed interest investigations were made on the still un-
utilized induline reactions in the naphthalene series and were
obtained with the help of the highly developed sulphonation
technique—uniform, red colouring sulphonic acids faster than
"Acid Fuchsine" and of equally perfect "equalising power"
with the archil-substitute "Azocarmine" (*Bad. Anil. Sodaf.
D.R.P.* 1888 *No.* 45370 *C. Schraube*). But the knowledge of
the constitution and the mode of formation of the red, violet and
blue Indulines was still lacking.

The key to the entrance into this group was lying with the
knowledge of structure of the Azophenine (*Kimmich, Ber.* 8,
1028; *Witt, Ber.* 10, 1309; *Ber.* 20, 1538). One had often
observed the behaviour of this substance known since Baeyer's
first investigations of the nitroso compounds in the initial stages
of the induline process (*N. Handwb. Chem. "Indulin", H. Caro,*
1880, *Witt and Thomas l.c.*). And it was also known that by
heating first a violet and then the brilliantly flourescing blue
Fluorindine was derived from it. Its constitution was however
insufficiently elucidated. Now it was proved to be an aniline
derivative of dianilidoquinone which had been discovered by
Hofmann a quarter of a century ago (*Hofmann, Proc. Roy, Soc.*
1863, 13, 4; *Zinke, Ber.* 16, 1555; *Ber.* 18, 785; *Nietzki and
Schmidt, Ber.* 22, 1655) and in the mean time had also been
closely investigated by Zincke. Azophenine was proved to be a
dianilido-quinonedianil; acids decomposed it again into aniline
and dianilidoquinone. Witt's crystalline Fast Blue, the Induline
6B, the bluest commercial product, produced therefrom by heat-
ing with aniline, now at once made an explanatory experiment
appear possible. In the structural formula of an Induline first
established experimentally, a phenazine ring as a binding struc-

tural unit was proclaimed.. The aniline molecule entering the Azophenine effected the phenazine linkage as it had happened two years ago with the formation of Safranine from Indamine explained by Bernthsen—the nitrogen atom intrlocking two benzene rings.   However, the paraquinonediimide nature of the quinone dianil remained intact.   In this induline ring both the ring-forming nitrogen atoms do not appear in a bond, and in the weakly basic and oxygen-free induline base the phenazonium group does not therefore predominate.   For the close establish- ment of the formula, however, the composition of the six benzene nuclei containing Induline was too complicated and also in the other most ill characterized Indulines of the benzene series no definite proof of the degradation or synthesis of the dyestuff molecule could be expected.   •

But then the course of investigation took another lucky direction.   In the naphthalene series already a compound of simple composition as the Azophenine, existed.   Its origin may be traced back to the experiments of Griess and Martius for the synthesis of artificial Alizarine from dinitronaphthol.   By heating the diaminonaphthol discovered by them, with aniline the anilido- naphthaquinoneanil of recent times, and at first investigated in Baeyer's laboratory, was obtained (*Ber.* 13, 123; *Ber.* 21, 391). This beautiful substance is derived through numerous processes analogous to those of the Azophenine.

By melting this naphthalene derivative or its components from the series of nitroso, quinone or aminoazocompounds with aniline hydrochloride and aniline, the beautifully crystalline red Phenylrosinduline, the dye base of the sulphonated Azocarmine was now formed.   If however, one of these components, benzene- azo-<-naphthylamine, the oldest mixed aminoazo-compound of Peter Griess (*Griess,* 1864, *Phil. Transact.* 3, 679) was heated with aniline in alcoholic solution, then the simplest member of this dyestuff family—Rosinduline, poorer in phenyl, was formed. Both of them when heated with hydrochloric acid—the phenyl- rosinduline by the elimination of aniline, the rosinduline by the separation of ammonia furnished the same oxygen containing Rosindone, which is similarly related to rosinduline as quinone to quinonimide.   From the Rosindone Baeyer's zinc dust method

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led again to the mother, substance, the α-naphthophenazine, which Witt had previously obtained from β naphthaquinone and orthophenylenediamine (*Witt, Ber.* 20, 571). By distillation the phenyl group attached to the linking nitrogen atom is detached as benzene.

After this successful excursion into the field of naphthalene the attention for investigation of the incomparably more difficult Benz-induline was sharpened. Success was soon attained by suitable melting conditions and separation processes to obtain from aminoazobenzene and aniline hydrochloride, the simplest red-violet Induline, $C_{18}H_{13}N_3$. Its derivative Phenylinduline, phenylated in the para-amino group, is formed directly by heating azophenine hydrochloride with intramolecular orthocondensation or by the elimination of an amino group of a technically prepared aminophenylinduline, a constituent of the oldest water-soluble Induline from aminoazobenzene |*Höchster Farbwerke, D.R.P.* 1889 *No.* 50584, (*Indamine*)]. From these Indulines was then obtained Benzolindone analogous to Rosindole and finally by zinc dust distillation, under splitting up of benzene, Phenazine the mother substance of the Benzolindulines, Eurhodines and Safranines was obtained.

For the Fluorindine formed from Azophenine by heating at higher temperature investigators had proved a double phenazine linking from the contiguous anil and anilido pairs of grouping of this dianilidoquinonedianil. This Fluorindone was known at the same time as the diphenyl derivative of the simplest homo-fluorindine obtained from former technical experiments from orthophenylenediamine and orthodiaminophenazine. That di-aminophenazine (*Otto Fischer and Hepp, Ber.* 22, 355) was however, the oldest phenazine derivative obtained from a smooth synthetic and typical reaction: The Ruby Red, in its etherial base-solution green fluorescing oxidation product which Peter Griess (*Ber.* 5, 201) had observed already in his successful discovery of the orthophenylenediamine. We have already seen that Phenazine and Naphthophenazine are derived from this orthodiamine.

Of the numerous new condensations of the orthodiamine in the domain of dyestuff chemistry the synthesis of Rosinduline

and Rosindone only may be considered here. Recently Kehrmann and Messinger (*Ber.* 24, 58) presented these through the action of phenylorthophenylenediamine on oxy- ∝ -naphthaquinoneimide and oxy- ∝ -naphthaquinone—the former " isomeric Alizarine " of Griess and Martius—in confirmation of the formula already stated by Otto Fischer. Thus grows the new fruit from the old germs.

Although the scientific work in the field of Induline was to be accomplished for a considerable time it has already greatly furthered as ever the industrial progress. The constitution of idigo and blue wood substituting Indazine (*D.R.P.* 1888 *No.* 47549; *Otto Fischer and Hepp, Ann. d. Chem.* 262, 263) and Indamines being known, one accounts for the working processes of paradiamines (*Otto Fischer and Hepp, Ber.* 23, 840) in the production of aminated Indulines and prepares systematically dyestuffs of the benzene and naphthalene series. Many new and valuable commercial products have already appeared in the market. Great industrial results can still be expected here.

Oxazines :

Already in the briefly described way, the first insight into the ring forming structure of azine and thiazine dyestuffs— Safranine and Methylene Blue had been gained; it was now considered to investigate the representatives of the Oxazines. Ring closure through oxygen was already known in the dyestuff groups of Phenolphthalein anhydride and the Xanthone.   From the oldest experiments with nitroso-compounds and phenols, even some valuable dyestuffs had continuously resulted. The reaction product of nitrosodimethylaniline and β-naphthol, described by Meldola in 1879 (*Meldola, Ber.* 12, 2065) appeared as a fast or new blue in the market and Gallocyanine from nitrosodimethyl-aniline and gallic acid, discovered by Horace Koechlin, had been prized as a mordant dyestuff. In 1888 Nietzki (*Ber.* 21, 1740) claimed both of these products as members of the oxazine group. Soon afterwards Weselsky's resorcin and orcin dyestuffs also were explained in a lucid way through comprehensive investigations by Nietzki (*Ber.* 22, 3020; *Ber.* 23, 718). In a synthesis of the Diazoresorufin from equal molecules of nitroso resorcin

and resorcin confirming Baeyer's original supposition Nietzki could observe in the first reaction phase the formation of an Indophenol and then its conversion into the oxazine dyestuff through the formation of the anhydride which occurred between the hydroxyl groups in the ortho positions to the diphenylamine-nitrogen. By further synthesis from nitrosophenol and resorcin or from nitrosoresorcin and phenol, and even more decisive through joint oxidation of amino resorcin and phenol the assumption of the oxygen linking was proved. As another compound of the oxazine group appeared now the Phenazoxine or Phenoxazine, which Bernthsen had obtained in 1887 (*Ber. 20,* 942) from ortho-aminophenol and pyrocatechol and had recognized the oxygen bond corresponding to his thio-diphenylamine. To this group are included many other dyestuffs, among which the Nile Blue produced from ⍺-naphthylamine and the nitroso-compounds of the alkylated meta-aminophenol deserve special mention.

Dyes Staining Bacteria :

The discovery of this dyestuff and its preceding Rhodamine is to be traced back to that impulse, which the development of the dyestuff industry had so often received from its practical applications. Yet this time the stimulus did not come from the circles of the big dyers who were always on the lookout for dyestuffs suitable for the fibres they wanted to dye. It came from the solitary investigators who establish with the help of the microscope the secrets of life-processes, disclose a world of invisible enemies and thereby furnish the scientific foundations for the art of healing. In the hands of the histologists, bacteriologists and their kindered, a highly developed staining technique also had grown up since the discovery of the aniline dyes. From the sparing use of insoluble pigments one had advanced to the visible range, to the differentiation of the finest as well as most ramified microscopic structures with the help of intensive, soluble, easily applicable and chemically sharply characterized specific coal-tar dyes. Contrary to big scales one dyed here on a small scale, mordanted, coloured intensely, made double colourations, discharged the colour or revived, and decolourized, till a clear,

many-coloured sample was obtained whose matching lines were now easy to follow. Who does not know, how Koch with the help of such dyes discovered the fearful bacilli of tuberculosis and cholera? Methylene Blue served him well. Ehrlich used the same dyestuff, (*Prof. Dr. P. Ehrlich, Deutsche Medicin. Wochenschr.* 1886, 49; *Bernthsen, Ann. d. Chem.* 230, 164) to investigate the function of the living nerve-substance. He found that only Methylene Blue and its derivatives, which had shortly before been obtained by Bernthsen, stained the ·living nerves. The Indamine described by Bindschedler and which was not linked through the sulphur atom, proved to be ineffective and the same was the case with the members of the triphenylmethane group and other aniline dyes. The investigator was pressed by the question: Why does Methylene Blue dye the nerves? Is the unique power conditioned by its ring-forming structure? Or, is it conditioned by the characteristic sulphur atom? Already in 1886 the structural knowledge had surpassed the narrow circle of specialists to such an extent that Ehrlich with full mastery of the theoretical dyestuff chemistry could challenge the industry to answer his question. He asked the industry to prepare the oxygen analogue of the Methylene Blue—according to present day nomenclature, the corresponding Oxazine—in an analogous way to the Toluylene Red · solved at that time from nitroso-dimethylaniline and meta-oxydimethylaniline. For the preparation of this still unknown starting material the meta-amino-dimethylaniline obtained shortly before by Groll (*Ber.* 19, 198) from dimethylaniline according to Hübner-Frerichs-Noelting's method of nitration showed the way (*Hübner and Frerichs, Ber.* 10, 1716; *Noelting and Collin, Ber.* 17, 261). From that one could arrive at the desired oxy-derivative through Griess' method.

The experiment was made, and once in possession of the resorcin analogous alkylated meta-aminophenol, the industry, at once discovered its eosine-like phthalein: the splendid light-stable Rhodamine, the basic counterpart of the oxygen-linked Fluorescein. Then the improvement of the rhodamine group and its related compounds was followed by (*Bad. Anil. Sodaf.* 1887, *D.R.P. No.* 44002) the discovery of industrial methods for the preparation of meta-aminophenol and later by the Nile Blue and

a series of other Oxazines.—A memorable reciprocity between practice and theory!

Azo-Dyes :

On our round through the investigated domain of dyestuffs from those of the azine groups we reached finally the numberless derivatives of the azo-benzene, its homologues and analogues. In this our greatest and still endlessly extendible groups of azodyestuffs—the oldest components of Induline, Safranine and Methylene Blue greeted us again. But here the double bonds of their linking pairs of nitrogen were not taken away. From' the amino-azo-naphthalene, discovered by Perkin in 1856, we turn back at the same time to the year of birth of the aniline dye industry. After two decades there followed the unexpected and mighty development of this group. The development in the domain of azo-dyestuffs to which up to 1876 only triamino-azobenzene or Phenylene Brown and the corresponding derivatives of azo-toluene belonged, dated from the successful introduction into the industry of Witt's diamino-azo-benzene or "Chrysoidine" and Roussin's sulphonated naphthol dyes or "Poirrier's Orange". What in 1877 released the potential energy with the quickness of thought in this field, was the glowing explanation given by Hofmann on the mode of formation of Chrysoidine and of Roussin's dyestuffs.

Witt's process was the first industrial utilization of Griess' synthetic method. But the basic Chrysoidine could stimulate only an expectation for the substitution of the costly Chrysaniline. In its applications it followed the closely related Phenylene Brown and the well-known basic aniline dyes. Roussin's products were on the other hand acid dyestuffs, of a pioneering new industrial significance. At once they were recognized as successful opponents of natural dyestuffs. They dyed in an acid bath the unmordanted animal fibres replacing Fustic and Flavine, with Eosine the scarlet red cochineal shades were obtained. As a new element the sulpho-group prevailed in them. As a valuable new addition they presented the dye industry with the sulphanilic acid, and the naphthols in their isomeric forms, every form causing its particular effect. Completely new was the technique of β-naphthol.

The explanation given by *Hofmann* (*Ber.* 10, 213, 1978) of the processes and products still mysterious and new to most people, which were followed soon by Witt's communications (*Witt, Ber.* 10, 350, 654, 1509) on Chrysoidine and 'Tropaeoline' discovered by him, disclosed first to the entire industry the glance on the limitless field of azo-dyestuffs. The source of energy to its racing development was based on the diazo-compounds of Peter Griess, and the province of aromatic amines and phenols made fruitful during the twelve years of Kekule's benzene theory [*Griess, Cf. particularly Ann. d. Chem.* 137, 39; *Phil. Transact.* 1864, 111, *and Emil Fischer, Ber.* 24, *Ref.* 1058. *Cf. the same, Hofmann's Biography of Peter •Griess and Caro's exhaustive sketches of Griess' methods*]. On the coupling of the diazo-compounds with amines or phenols through the stable bond of the azo-group depended the essence of "Griess' method."

Everything was given here through theoretical investigation. Already in 1866 Kekule' himself had established the constitution of the diazo and azo-compounds. (*Kekule's Lehrbuch der Organischen Chemie* 2, 715, 689). There were numerous diazo-amino-compounds, and also their transformation into the stable amino-azo-compounds have been elucidated by Kekule' (*Zeitschr, f. Chem.* 1866, 689). Well known were oxy-azo-benzene and phenol-bi-diazobenzene, the first representative of the disazodyestuffs; Griess had been even aware of the dye character of both the compounds (*Griess, Ann. d. Chem.* 131, 88). The oxyazo-benzene was directly sulphonated (*Tschirwinsky, Ber.* 6, 561). A large number of applications of Griess' method was also recorded in the scientific literature. Griess himself had prepared our present benzene-azo-α-naphthylamine from diazobenzene nitrate and α-naphthylamine. Kekule' (*Kekule' and Hidegh. Ber.* 3, 233) and Baeyer (*Baeyer and Jäger*, 8, 151) published in collaboration with their students synthesis of oxy-azo-benzene and dioxy-azo-benzene through the coupling of diazo-benzene nitrate with phenol or resorcin in alkaline solution. By a renewed coupling of oxy-azo with diazo compounds Griess had produced (*Griess, Ber.* 9, 627) the corresponding disazo-compounds and thereby referred to the applicability of sulphanilic acid and of the "self-evident great number" of azo-compounds that could be prepared synthetically. The communication of

routine experiments appea¹ed to the great investigator to offer no more "new chemical interest"T·'ü the fruit of year-long self-less and joyful investigations slumbered in his bosom. Even a homologue of Chrysoidine had been discovered over a year ago (*Hofmann, Ber.* 10, 388; *Witt, Ber.* 10, 654). Everything was ready to break into bright flame but there was no igniting spark, the creative work. The first industrial utilization of the scientific discoveries was lacking.

Sulpho-Acids :

Three ways were now offered to the industry for the production of water soluble acid dyestuffs. One could introduce the sulpho-group into the amine which was to be diazotized, or into the amine or phenol used for coupling or into the previously formed spirit-soluble amino or oxy-azo-compound. At that time these ways appeared still equally valuable and the influence of isomerism was hardly suspected. It was generally believed that the acid character of the dyestuff depended on the number of sulpho-groups introduced into the molecule. One had models only in the water-soluble Aniline Blue and Induline. All the three ways were tried simultaneously. But even in spring, 1877 the opinion was still prevailing that the azo-group could furnish to the molecule which it occupied. a yellow colour only (*Witt, Ber.* 10, 876). From the sulphanilic acid one ascended to its homologues and noticed the increasing red colour-tone of its azo-dye-derivatives. Still one step further—and one grasped the analogies, to the sulphonic acids of then only accessible ∝-naphthylamine. From its combination with β-naphthol resulted in summer, 1877 the first red and valuable azo-dyestuff, rightly named the "Fast Red" (*Bad. Anil Sodaf. D.R.P.* 1878 No. 5411, *H. Caro; Griess, Ber.* 11, 2199). Already in the same year the dye industry welcomed it as the first serious opponent of the Cochineal and of the lac dye for the production of their dark red shades in combination with the Archil. But out of the combination of ∝-naphthol however, resulted surprisingly a yellowish brown dyestuff, the 'Fast Brown'. Soon the Fast Red was followed by an identical compound "Roccelline" prepared in the same way as by Roussin and Poirrier. These were the oldest azo-dyestuffs of the new epoch, built up from naphthalene only.

JOHANN PETER GEUSS (1829–1888)

JOHANN PETER GRIESS

1829 — 1888

Every student of organic chemistry knows what diazo-reaction is and what a great role it plays in the organic synthesis and in the manufacture of dyes. This remarkable reaction was discovered by Peter Griess in 1858. He was a German chemist empoyed in an English brewery and carried on researches on his favourite line of diazotisation in his spare time. It is an irony of fate that the reaction discovered by him which proved of immense economic significance in dyestuff industry could come to no personal benefit to him. The profound influence which his researches exercised on the development of organic chemistry was fully recognized by the contemporary chemists. This is evident from the brilliant descriptions of his life and work published after his death by the renowned chemists, A. W. Hofmann, Emil Fischer and Heinrich Caro in the *Berichte der deutschen chemischen Gesellschaft* of 1891. Caro has rightly said that had Griess discovered nothing else than the diazo-reaction this would have been sufficient to make his name immortal for all the time to come.

Griess was born on the 6th September, 1829 in a little village near Kassel. His father possessed a small farm which he managed himself The young Peter in his early years showed an intellctual bent of mind and aversion for agricultural pursuit. After finishing his school career he took his first lessons in chemistry with Kinkelblech at Kassel. He then attended lecture at the University of Jena and then at Munich came in close touch with Liebig. Afterwards he went to Marburg and worked with the famous chemist Kolbe. In Marburg under the inspiration of Kolbe Griess first studied the reaction of nitrous acid on aminobenzoic acid and obtained fruitful results. In 1858 Kolbe introduced Peter to Hofmann who immediately recognized the merit of his work. Hofmann offered him a post of his assistant in the Royal College of Chemistry, London. Here Griess worked with indefatigable energy on his favourite line—The Study of the action of nitrous acid on amino-compounds—which proved to him as recreation and breath of life (*Erholung und Lebensluft*). He used to work from morning 8 to late in the night and even on Sundays when all others had gone out Griess was found to work in his laboratory. From Royal College of Chemistry he secured a job in the brewery of Alsopp & Sons in Burton, in 1862, which post he held for about a quarter of a century working in this firm's laboratory for 6-7 hours daily but the results obtained in the laboratory of the brewery he was forbidden to publish. The rest of the time he worked in his private laboratory on the diazo-chemistry.

As has already been mentioned he could not improve his financial position by the discoveries. No doubt he took some patents but others reaped the benefit of his discovery. The great significance of his work has been described by Emil Fischer in the following terms :—

"The brief and precise form stands in contrast with the

abundance of factual data. This corresponds perfectly with the procedure of work of the author. Gress owed his astounding success to this experimental talent of the very first order and not to new and far-reaching ideas or particularly lucky chances but mainly to his keen observations and consequent unceasing pursuit of the phenomena."

In the mean time the German patent law had started and in the wake of Methylene Blue and Acid Fuchsine began the series of dyestuff patents from 1877. After the unveiling of the secret of the 'Naphthol Orange' one was asking how the sulpho-acids of Rosaniline would behave in place of the sulphonated aniline. These acids were still unknown; what could one expect from them? The sulphonation of the water soluble Fuchsine must appear meaningless; its acid sensitiveness made one expect at most the yellow dyestuffs to be of the acid rosaniline salts. The big azo-dyestuff molecules obtained therefrom showed curiously enough only a very little affinity for the fibre. But still more striking was the fuchsine-like colour-tone of the strongly sulphonated fuchsine, its complete acid stability, its perfect colouring capacity, its ability to produce 'mixed colours' with all acid dyestuffs in the same acid bath, like the wood dyes, the Indocarmine and the Archil. Very soon the Acid Fuchsine was followed by the Fast Yellow obtained through direct sulphonation of the amino-azo-benzene (Bad. Anil. Sodaf. 1877 Fr. Kochler; Gracssler, D.R.P. 1878 No. 4186) as a substitute for the fustic for the quercitron and the curcuma. And after the discovery of the Malachite Green followed the brilliant series of green, blue and violet dye-stuffs of the triphenylmethane group. So the first appearance of the acid dyestuffs in the domain of azo-dyes had already exercised their reflex action on the development of the oldest neighbouring field. But the first experiments to introduce the sulphonic acids of the Alizarine and Purpurine into the dye industry also date from that epoch.

The oldest German azo-dyestuff patent, enacted in 1878 simultaneously with that of the Fast Red (Griess, D.R.P. 1878 No. 3324), bore the title: Peter Griess, and dealt with the "Preparation of Dyestuffs by Coupling Compounds of Diazo-phenols and Phenols." The simple rules of manufacturing of the unique industrial "Methods of Griess" had been explained so clearly by its discoverer that later investigators could be satisfied with quoting of the 'components' tried by him, of course there were many, still untried by Griess. The constructive character of the modern dyestuff investigations appeared earliest in this domain. To name the azo-pairing or coupling of the components one lent the notation "Coupling" even from a constructive idea

of the mechanics. The truly inventive moment could express itself no more even here in the foot steps of the trodden path, no more in the thousandfold, methodical preparation of new azo-compounds; only in the discovery of a valuable product, only in the sure distinction of the gold grain from the sand, the genial eye of the lucky discoverer would manifest itself [*Cf. The Decision of Reichs Court i/S. Congo Red Patent; Patent literature,* 1889, 209; *Doctrine of the new technical effects*]. Such gold grains were not found amongst Griess' diazo-phenol dyestuffs. They were abundantly found however, in the follow-ing patent on the preparation of dyestuffs from the disulphonic acid of β-naphthol (*Höchster Farbwerke, D.R.P.* 1878 No. 3229, *H. Baum*).

Through the epoch-making discovery of this patent, the industry was first shown the way to a series of scarlet dyestuffs, which in ever cheaper and more perfect form emerged from the workshop and replaced almost completely within ten years the Cochineal in its applications in wool dyeing industry (*Cf. Lehne, Färberztg.* 1890/91. 20). As the diazo-components of those first "Ponceaux" (Poppy colour......Fr.) served aniline and its homologues, particularly xylidine up to cumidine produced by the method of Hofmann's atomic rearrangement. With its increas-ing molecular weight the colour tone increased from the most yellowish to the most bluish red. Soon Griess added to these diazo-components the diazo-anisole, their homologues, analogues and sulpho-acids (*Griess, E. P.* 1878 *No.* 4726; *Bad. Anil. Sodaf., D.R.P. No.* 12451: *Höchster Farbwerke No.* 7217), after he had learnt that his first diazo-phenoldyes owed their alkali sensitive-ness to the free hydroxyl groups and that through the introduc-tion of alkyl groups the colour shade turned from yellow to red. In the mean time, the diazo-compounds of the amino-azo-benzene, their sulpho-acids, homologues and analogues furnished a direct and greater progress. The proof of their normal reactivity was followed immediately (*H. Caro and Schraube, Ber.* 10. 2230) after their introduction into the industry although only later patents gave evidence of it [*Bad. Anil. Sodaf. U.S. Am. Pat. No.* 224927, 224928 (*Fr. Koehler*): *Krugener Höchster Farb-werke D.R.P.* 1879 *No.* 16482: *Graessler, D.R.P.* 1879 *No.* 16483]. A new series of intensely coloured scarlet red disazo-dye-

stuffs were prepared which contained two azo-linkages differently grouped than the former disazo-compounds of the type of phenol-bi-diazobenzene. In the three membered chain of these disazo-compounds each part could be replaced through another of its allies if first one seized the "mixed amino-azo-compounds." An endless play of combinations was opened here to the industry. The shades became still deeper and darker the higher one ascended to the series of the compounds richer in carbon. While from the disulphonic acid of the amino-azo-benzene by combination with β-naphthol the Biebrich Scarlet resulted (*Nietzki, Kalle & Co., Ber.* 13, 800), so one met already a brown violet archill-like dye-stuff in the analogous combination of the amino-azo-xylene (*Bad. Anil Sodaf.* 1881, *Archil Red, Schunke, U.S.A. Pat. No.* 246221). And as finally one turned completely to the naphthalene series by coupling first diazotized sulphonic acids of β-naphthylamine with α-naphthylamine and then the so formed derivative of amino-azo-naphthalene with naphthol-sulphonic acid, the black colour of the log wood was obtained. The first Blue Black [*Bad. Anil. Sodaf.* 1882, '*Blue Black*' (*C. Glaser*): *Cassella & Co., D.R.P.* 1885 *No.* 39029 (*Hofmann and Weinberg*); *Elberfelder Farbenfabr.* (*Diamond black on chrome mordant*). *D.R.P.* 1889 *No.* 51504] became itself the starting point for important improvements in the disazo series of the Naphthol Black, Brilliant Black, the Diamond Black and their numerous related compounds. Whilst since 1882, since the conversion of β-naphthol into β-naphthylamine-sulphonic acid, the diazo compounds from β-naphthylamine-sulphonic acid becoming gradually more accessible by simple coupling have led to new scarlet red naphthol dyestuffs. Also a useful archil substitute of Roussin (*Roussin & Poirrier, D.R.P.* 1878 *No.* 6715) resulting from the diazo-compound of paranitroaniline in combinatoin with the naphthionic acid of Piria appeared in the market. In their circle of acid dyestuffs, which fought successfully with the natural products. Roussin's and Poirrier's oldest Diphenylamine Orange proved particularly useful besides the β-napthol Orange. The "Bordeaux Red" from diazo-naphthalene and the β-naphthol-disulphonic acid had soon joined the Fast Red. From these few examples one can easily see the amount of zeal manifested in the investigation mainly in the field of the applicable diazo-com-

pounds. Into these works shone the light of numerous communications of Peter Griess, in the *Berichte*, although some of his suggestions found their fruitful ground in later years only.

However the oldest Scarlet patent had also lastingly furthered the development of the azo-dyestuff industry towards another direction.

From the choice and character of both the isomeric *β* -naphthol-disulphonic acids, 'R' and 'G' of the patent, one had learnt for the first time the far-reaching influence of the position and number of sulpho-groups on the dyestuff character. In combination with the same diazo-compounds two different red and yellow series of dyestuffs resulted from the two isomers. Also the combining capacity of both the acids was different, so that soon afterwards one could establish methods of separation. The influence of isomerism, became still more visible now when the sulpho-groups were not added to the naphthol but to the diazo-compounds or when even the spirit-soluble dyes were sulphonated. In the alizarine industry, in the anthraquinone sulphonic acids only the preparation and separation of the uniform sulphonic acids had been established by that time. Now the knowledge of the great industrial value of such uniform materials filtered also into the province of azo-dyes.

The next consequence was the separation of the mono-sulphonic acids of the *β* -naphthol. From "Schäffer's Acid" which had been known since the year 1869, its much more valuable isomer, the *α*-monoacid of *β*-naphthol was separated in 1881 [*Elberfelder Farbenfabriken, D.R.P.* 1881 *No.* 18027; *E. Frank* 1883 *No.* 26231 (*Separation through Diazo compounds, see Pfaff*]. Then the conditions for its large-scale production and convenient method of separation were investigated. Its new dyestuff derivatives appeared in the market. The combination of the diazo-compounds of the sulphonated amino-azo-benzene and toluene proved to be the most successful "Crocein dyes." These brilliant Crocein Scarlet dyes with the help of mordants found entrance also into the cotton dyeing industry. Soon a memorable Patent process (*Decision of the Reichs Court of the 13th July,* 1885) for the development of the German Patent Law directed the interest of science and practice to the new industrial progress

and carried the knowledge of the sulphonation technique to a large circle of human society.

In 1883 it was also found that along with the useless Schäffer's sulphonic acid of α-naphthol an extremely valuable isomer was formed which could more easily be produced from Piria's naphthionic acid by the method formerly employed by Nevile and Winter. The combinations with this α-mono-sulphonic acid of α-naphthol showed [*Verein Chem. Fabr. Mannheim, D.R.P.* 1883 *No.* 26012 (*O. Witt*) *Dahl & Co. (Gaess)*], contrary to those of their Schäffer's isomers, the character of acid-fast azo-dyestuffs and they are red to violet, instead of yellowish brown. "Fast Red C", "Azorubine", "Brilliant Ponceau", "Double Scarlet", Azoarchil and other new varieties appeared in the market. Later it was recognized (*Witt, Ber.* 19, 1722) that here the sulpho-group of the azo-compound had prevented its entrance into the para position so much preferred by it. Ortho-azo-dyestuffs were formed as in the isomeric series of β-naphthol and on this question of position an explanation was then found for their beauty far surpassing the para-azo-dyes of α-naphthol and its Schäffer's acid and for their indifference against acids and alkalis (*Liebermann, Ber.* 16. 2858; *Zincke and Bindewald, Ber.* 17, 3026).

Of both the disulphonic acids of β-naphthol, industrial interest was taken at first only in the 'R-Acid', closely investigated by Griess (*Griess, Ber.* 13, 1956). With the progressive development of the naphthol-dyes in 1884 here also a more productive method of preparation of the uniform 'G' or τ-isomer was discovered, which led to a series of dyestuffs of great purity of shade and pronounced crystallizing power [*Cassella & Co.* (*M. Hofmann*) *D.R.P.* 1884 *No.* 36491, *Höchster Farbw*]. The representative of this group was the "Krystal Ponceau" derived from its combination with the diazo-compound of α-naphthyl-amine.

Unceasingly the industrial investigation continued further along the path of the isolated isomers once so successfully started. One turned simultaneously to both the directions: to the diazo-components and to the phenols and amines, above all to the investigation of the still new field of naphthalene whose significance

became daily more convincing. Griess' method with its quanti-
tative results, its few claims on the equipment of manufacture
and on the industrial experience—only diazotizing and mixing
vessels, boiling vats, filter press, drying chambers, ball mills—
could bring into reach the introduction of valuable and cheap
substitutes of natural colouring matters even to the uninitiated!
More than ever one now organized scientific mass production in
the industry. On the already known derivatives of naphthol and
naphthylamine new isomers or higher sulphonated members were
added. One advanced further to the diazo-naphthalenes and
amino-naphthols, and found that the "alizarine position" of the
hydroxyls in the ortho and peri-positions (*Witt, D.R.P.* 1889
No. 49979, 49872; *Bad. Anil. Soda]*. 1889, *No.* 51559) bestows
also to the azo-compounds mordant dyeing and milling-fast pro-
perties, even the carboxyl group imparting the lake-forming
properties partly in combination with the contiguous hydroxyl
group and partly without it (*Nietzki, D.R.P.* 1887 *No.* 44170
Alizarine Yellow); Elberfelder Farbenf, (*Diamond-colours
D.R.P.* 1889 *No.* 51504 *Krekler and Lauch*, 55649.) One
observed also the beneficial influence of the subsequent mordant-
ing by metal and principally by copper salts, as well as by soluble
chromates, on the light, air and wash fastness of the dyes
obtained, or on the wonderful deepening of the colour shade
from the most illuminating red to the deepest black ("*Chromo-
trope*" *Höchster Farbwerke. Lehne, Färberzt.* 1890/91, 145).
Azo-dyes of beauty approaching the Acid Fuchsine and its
derivatives were obtained, as one turned to "Schöllkopf's"
α-naphtholdisulphonic acid (*Schoelkopf. Anil CO. D.R.P.* 1885
No. 40571) and from it through the partial caustic soda fusion
a peri-dioxynaphthalene-monosulphonic acid was obtained [*Elber-
felder Farbenfabr. (Duisberg & Ulrich) D.R.P.* 1889 *No.* 54116,
"*Azofuchsine*", *etc.*] But out of a symmetrical peri-dioxy-
disulphonic acid resulted the "chromotrope". And while caustic
soda fusion of naphthionic acid led to the valuable α-naphthol-
sulphonic acid, Laurents' isomeric acid derived from metanilic
acid according to the process of preparing meta-aminophenol
provided a new amino-naphthol (*Act. Ges. Anilfabr. Berlin* 1888
No. 46307; 1889 *No.* 49448) with which the diazo-naphthionic
acid was coupled into a blue dyestuff. However, as then one

obtained from 'G'-acid through ammonia by alkali fusion the
β -naphthylamine-disulphonic acid and through the corresponding
β -amino- α -naphthol-monosulphonic acid 'G', one discovered in
1889 its remarkable properties that two completely different
series of dyestuffs were formed according to the choice of com-
bining conditions with diazo-compounds. In one the amine
determined the entrance of the azo-group, in the other the phenolic
nature of the amino-naphthol. Hydroxylated β -naphthylamine
or aminated α-naphthol azo-dyes of great intensity and stability
were obtained (*Cassella & Co. D.R.P.* 1889 *No.* 55024, 55648
Diamine Black etc.). The aminated series permitted diazotiza-
tion of its free amino group and thereby again the synthesis of
a new series of dyestuffs—a property which soon became
important in the field of the substantive azo-dyestuffs (*Elberfelder
Farbenfabriken, D.R.P.* 1890 *No.* 53799).

Substantive Cotton Dyes :

This field was already opened to industry since the dis-
covery of Congo Red. The main point of that discovery
lay in the knowledge of a pioneering new technical effect. The
dyestuff dyed an intensive red on cotton without the use of
mordants. Such a property had never before been witnessed in
the groups of coal-tar dyes. Phenylene Brown, Safranine and
Methylene Blue tinged unmordanted vegetable fibre only to a
small extent, the rose coloured Succinein of the Rhodamine group
was not discovered at that time. Nature also did not supply
perfectly red substantive dyes, only light rose. shades could be
imparted by the costly Safroncarmin, yellow by curcumin and
orange by Orleans. The Catechu Brown was formed by oxida-
tion and mainly through copper salts and had thereby once given
the direct impulse. to the production of Mauvein, Aniline Black
and later the Methyl Violet. A great technical necessity pre-
vailed to replace the adjective red of Alizarine and wood dyes
by simpler and cheaper dyes for less important purposes. A
further demand was felt for dyeing simultaneously, mixed fibres
of half wool and half silk. To this demand Congo Red yielded
first. Its discovery proved again the theorem that only the
successful solution of a technical problem can open new paths

for the industry. For long before one had turned in vain to this dyestuff. The Congo Red patent (*P. Böttiger, D.R.P. 27th Feb.*, 1884 *No.* 28753) disclosed in 1884 first the knowledge of the substantive dyes of the tetra-azo-combinations of the para-diamine. The earlier English patent of Griess had not yet been published [*Griess, E.P. 9th January.* 1884 *No.* 1074. *The first experiments were of his student friend W'. Gerland in the factory of Steiner & Co. in Acrington.*] This patent contained the communication " That dyestuffs formed from the tetra-azo-diphenyl-disulphonic acid by double coupling with the naphthylamine whose sulphonic acids and derivatives, particularly with the naphthionic acid of Piria, possessed the valuable property to dye cotton fibre also without the application of mordants." Already in 1881 Griess had encouraged experiments with such dyestuffs in an English Turkey Red dye firm but the relationship of his products to the fibre proved too insignificant. Also scarcely any firm was previously lacking in azo-dyes from para-diamine (*Griess, Ber.* 17, 607; *G. Schultz, Ber.* 17, 461; *Witt, D.R.P. No.* 26012) yet they were tested only in acid bath on wool. The Congo Red had to be dyed in alkaline state, for even the carbonic acid of the air turned the colour brown and stronger acids converted the red to blue. Many a coal-tar colour industrialist rejected the acquisition of the patent, till finally the practical view of an experienced dyer provided the successful start of the sensitive indicator into the industry. In the dyeing processes an excess of alkali was left as protection. Yet with such protection the ambitious dyestuff industry did not long remain satisfied.

In comparison with Griess' compounds of poorly colouring property Congo Red was only slightly sulphonated. But just in this apparently small difference the merit of the lucky discovery was based. The intensely colouring dyestuff consisted of the combination of tetra-azo-diphenyl discovered by Griess with two molecules of naphthionic acid first tested by him as well. Besides the patent contained the application of all the isomers known at that time—mono or disulphonic acids of the ∝ or β-naphthylamines. Of these, however, little was known, and of none the structure was investigated with certainty, but the surprising success of Congo Red was sufficient to attack newly opened fields. At once one sought for substitutes for benzidine

and the well known sulphonic acids of the naphthylamine, realized all the experiences in the up to then manufacture of azo-dyes, attacked first the homologues, (*Toluidine, Duisberg, 1885. Elberf. Farbenf. Benzopurpurine, ·Deltapurpurine, D.R.P. No.* 35615, 1886 *No.* 42021; *Frank* 1884 *Chrysamine*) isomers and analogues [*Diaminostilbenesulphonic acid (Bender* 1886. *Leonhardt & Co. "Brilliant Yellow", Chrysophenine "Hess' Purpur" D.R.P. No.* 38735; 42466)] of the diphenyl base, found that only the para-diamine (*para-phenylenediamine, Schraube,* 1887. *Bad. Anil. Sodaf. "Violet Black D.R.P. No.* 42011, 42815) possessed the new mysterious property of forming substantive azo-dyes.   Every tetra-azo-compound was* coupled with all accessible. amines, phenols ·and their derivatives [*Salicylic acid. Frank,* 1884. *Elberf. Farbenf.*) *Chrysamine, D.R.P. No.* 31658. *α-naphthol-α sulfonic acid (Duisberg* 1885) *Azo Blue D.R.P.* 35341)], added methoxy [*Dianisidine (Duisberg* 1885) *Benzoazurine D.R.P.* 38802] and ethoxy groups [*Ethoxybenzidine (Weinberg* 1887. *Cassella & Co. Diamine dyestuffs) D.R.P. No.* 44209, 46134] in the diphenyl nucleus or linked them anew according to the method of benzidine sulphones [*Griess and Duisberg Ber.* 22, 2459, *Sulphonazurine; Diamino carbazole, ('Carbazole Yellow' Bohn* 1888. *Bad. Anil. Sodaf.*) *`D.R.P.* 46438], joined simple azo-dyes with free para-amino-groups by the application of phosgene [*'Cotton Yellow' Bad. Anil. Sodaf.* 1888 *D.R.P. No.* 46737 (*C. Müller*] or other binding material together, continued to the combination with· dioxy-naphthalene, amino-naphthols and their sulphonic acids, searched all the intermediate products and extended at the same time in previously unsuspected manner the scientific knowledge in the field of naphthalene.   Through the discovery made in 1885 [*Act. Ges. Anilf. Berlin. D.R.P.* 1885 *No.* 39096; *Martius. Ber.* 19, 1755; *Lunge, Ber.* 19, 1697] that by the formation of Congo Red both the diazo-groups of tetra-azo-diphenyl enter into the reaction one after another, and that the intermediate products first formed according to the manner of simple diazo·compounds, can couple with other amines or phenols; one succeeded also in the synthesis of any mixed or unsymmetrical azo-dyes as desired, and to which according to necessity one can incorporate systematically one or the other valuable property of their components! Thereby the

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already existing constructive activity in the field of azo-dyes
increases to infinite dimensions. .And still a further addition is
registered in 1887 through the appearance of Arthur Green's
Primuline in the market [*Green, J. Soc. Ind.* 1888, 179; *Dahl &
Co. D.R.P.* 1885 *No.* 35790; *Jacobson, Ber.* 22, 330; *Pfitzinger
and Gattermann, Ber.* 22, 1063; *Gattermann, Ber.* 22, 422, *Green,
Ber.* 22, 968]. A light yellow dyestuff was formed by the
sulphonation of a highly sulphonated para-toluidine, which fixed
itself without mordant on cotton fibre. It showed the peculiarity
that it could be converted on the fibre into an insoluble diazo-
compound which then by a passage through alkaline ß-naphthol
solution was at once transformed into brilliantly red wash-fast
azo-dyestuff. With other phenols or amines other correspond-
ing colour effects were attained on the fibre. Yet the secret of
the unpatented Primuline did not long remain hidden and the
'In-grain Colours' which were originated at that place in which
Nicholson had once worked with such conspicuous success—
everybody turned to the new direction and patents after patents
followed.· Scientific solution unearthed simultaneously a less
complicated and already known intermediate product—the de-
hydrothiotoluidine, an aminated homologue of its mother
substance being Hofmann's benzylaminophenylmercaptan.

. Yet the diazotizable dehydrothiotoluidine and its next higher
homologues became again the starting point for the synthesis of
new dyestuffs. By alkylation the beautiful yellow Thioflavines
were obtained (*Cassella & Co. D.R.P.* 1888 *No.* 51738); the
diazo-compound of the metaxylidine derivative being coupled
with an epsilon   -naphthol-disulphonic acid produced the
substantively colouring luminous 'Erika', [*Act. Ges. Anilfabr.
Berlin (G. Schultz)* 1888. *Anschütz & Schultz, ber.* 22, 583]
the representative of a series of substantive mono-azo-dyestuffs,
to which the dyestuff derivatives of the oxy-monoamino-diphenyl
(*Bad. Anil. Sodaf.* 1888 *D.R.P. No.* 52661, *G. Koerner*), of the
para-oxyderivative of .Hofmann's xenylamine also joined.   So
through "Primuline" the notion was shaken violently for the first
time that the properties of substantive dyes on the disazo dye-
stuffs from para-diamine must be limited. But in other sulphur-
containing compounds of aliphatic series also this property had

previously been contested: in the yellow coloured Canarine or Pseudosulphurcyanide, in the grey coloured *Cachou de Javail* and in the 'Rhodamine Red' of Nencki. Probably one is confronted by an absorption phenomena conditioned through the structure of the dyestuff which must disclose itself to later investigation. A still further information was disclosed by 'Primuline.' Its capacity for diazotization on the fibre led to a series of tinges obtained from substantive azo-dyes with free amino groups, which then, through diazotization and further suitable combination on the fibre could be raised to an Aniline-Black-like intensity and fastness. Then ever higher rose the dyers' demand for fastness of the daily increasing competitions of their natural colouring matters. The beginning in this direction was made in 1890 by the 'Diamine Black' formed from alkaline combination of tetra-azodiphenyl with β -amino- α -naphthol monosulphonic acid 'Ge'. The patent relating to this presented 48 components suitable for the conversion of the Diamine Black and its numerous analogues, almost all from the naphthalene series and of well known structure!—a convincing proof of the enormous development in this synthetic field. Removed to far distance the empiricism of the first dyestuff-melt appeared to us now.

Nevertheless, it is to that time and even further till to Perkin's that the origin of the production of azo-dyestuffs in the fibre is to be traced back (*Perkin, Chem. News*, 1861, 354; *Holliday, E. P.* 1880 *No.* 2757; *Lehne, Färberztg. I*, 46). Yet since the discovery of the naphthalene dyes only this direction gained a practical significance. Attempts were made to bring about the alkali insoluble and therefore soap-fast combinations of the β -naphthol, with the unsulphonated diazo-derivtives of aniline, its homologues and analogues by impregnating or printing the material with the components in successive operations. The first success was attained by Holliday in his dye works near Rouen, and further progress was made by the Swiss and Alastian Colourists. In the factory directed by Horace Koechlin in Lörrach remarkable results have been attained by Feer in printing and reverse printing in recent times. For impregnating cotton an alkaline solution of β-naphthol was used, and wool and silk were prepared with free β-naphthol; then followed the

imprinting of the diazo-compounds—from ˙ diazo-benzene upto the tetra-azo-diphenyl and its derivatives; particularly valuable effects showed the combinations of the naphthylamines. Though this direction took further course of development yet its influence accelerated already the striving for producing substantive dye-stuffs equally fast to light and water. The dyestuff technician must not yield to the dyer!

A closer view ₍of the immense territory of the azo-dyes must be abandoned now; we shall meet only the most approved representatives of this promising group, in their applications, partly alone, partly in combination with the ortho-nitroso and nitro-dyestuffs, which were first made available for the industry when their intermediate products the naphtholsulphonic acids were investigated, as also combined with the hydrazo dyestuffs, derived from their diazo-compounds: the Tartrazine, a substitute for ·Flavine (*Ber.* 18, 46; *Ber.* 20. 3146; *Ber.* 14, 2028; *Ber.* 20, 824).

Retrospection :

The laboratory director concludes—"now we have finished our round amidst the most important groups of dyestuffs whose synthesis presented itself so attractively in that exhibition cup-board. From their mother substances we saw the colourful off-shoots being formed and have recognized the relationship between their individual groups, families and series. We have followed the interwoven processes of development of their scientific knowledge through the last three decades. And this knowledge, we state it proudly—is in our opinion, the result of a national achievement. Therefore, a national industry has developed here. Every germ, which the industry presented, found—even far from the homeland—its fertile ground in German Science, we trace this blessing back to the School of·Justus von Liebig. Both the discoverers whose joint names are greeting us at the entrance of the factory, were influenced by the great master's teaching; the joint pictures of those discoverers have also greeted us in the national gallery (*dedicated by the German Coal-tar Colour Industry,* 1890). Hofmann and Kekule',—each investigating in his own particular manner, each founding his own school, which

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carries forward the spiritual impress of its first founder through generations of students. From the field of aniline opened up by Hofmann, the oldest aniline and azo-dyestuff emerged, the empirical discovery of dye-stuffs was followed by its scientific explanation, their structural knowledge was the later fruit of the benzene theory. From the knowledge of the structure, however, developed the synthesis, to which the present industry owes its constructive methods of work and its astonishing mass production [*in England were granted from 1856-66, 141 patents, from 1866-76, 59 patents on Coal-Tar Dyes, thus an average of ten per year. On the other hand an average of annually 132 German Patents were granted in the years 1889-1890. The work of Friendländer, contains 431 from 1877-1887 and 374 from 1887-1890 published German patents on Coal-Tar Products*]. Every new discovery now directs the view on far extending dyestuff series, and all hands, all helping agents are ready to exploit the new field. These are achievements of the German researches which combined with German mental outlook in the frame work of the progressive unfolding of German trade and commerce, must preserve the national character of the native coal-tar industry—as long as in their veins the hitherto existing reciprocal action of theory and practice pulsates! The expiry of our monopolies are not to be feared. Newer and better things succeeded the old ones, and still in endless distance appears our goal, the complete displacement of natural colouring matters (*Cf. Import Statistics of Indigo, Wood dye, etc., Lehne's Färberztg. 1889/90, 372 and the export of indigo from India, do. 345*).

Application of Dyestuffs :

Let us now cast a glance on the application of our dyes:

We hurried through working halls of the test dyers, who test the conformity of manufacture with the preserved types and who follow the progress of competition by the investigation of the daily arriving commercial samples. Also the new laboratory product passes here the foretest of its technical quality.

Further on, the way led us to the sample dyers (Cf. specially: Möhlau, *Organische Farbstoffe* ; Hummel-Knecht, *Färberei etc.*; Kertesz, *Anilinfarbstoffe* ; Gentele, *Farbenfabrikation* ; v. Perger,

Mitteil. Technol. Gewerbe-Museum, Wien). The first glance on the extensive workshops aroused in us the impression of a perfectly equipped model dyeing and printing works, all helping agents of the modern dyeing technique were here combined. We passed the series of steaming kettles in which all spun up fibres from the loose to the artistically woven ones were dyed, the dyeing, spilling and wash machines, centrifuges and drying chambers, and entered the printing room with its hand and Rouleaux printers, its continuous ageing apparatus and its steam cylinders. We also looked into the workshop where the paper broth was dyed and formed up to the finished paper in glasses or even in the cylindrical paper mills; we then saw how the brilliant spirit lakes were produced from spirit soluble azo-dyestuffs, how leather was imparted with every kind of colour from the lightest fashionable shades to the full leather brown or deep black—how horn, ivory-nut, straw, wood, grass, hides and feathers were dyed. We then entered the laboratory of the pigment making chemists who prepared and tested artificial dye-lakes for the wall-papers, posters, book and art printing, for the lithographer and the painters and for hundredfold other useful purposes. We now received explanation of the nature of our coloured inks and India ink, of the chemical causes of the after-darkening of iron gallic acid items [*Schluttig and. Neumann, Eisengallustinten Dresden, v. Zahn* (1890)]. We observed also the photographer during the development of his pictures with hydroquinone and 'Eikonogen' and found that even the cosmetic of hair-dyes (*H. Erdmann, D.R.P.* 1888 *No.* 47349; 1889 *No.* 51073) were enjoying an addition through the para-diamine, para-aminophenol and quinone —in short, an almost bewildering picture unfolding itself in all directions—a picture of the colour producing applications of the tar derivatives and of the demand of colours which they satisfy since the discovery of the first aniline dyes in a manner changing previous attempt and which they increased to an unexpected height. By this increase, jointly with the incessantly progressing culture and the higher standard of life, the natural dyestuffs also would necessarily find a more extensive application. "And this explains " remarked the instructing colourist, " why the still undiminished and even increased total consumption of Indigo, wood dye, and extracts of catechu and of the tannin containing pro-

ducts, don't give us a correct idea as to how great a damage the coal-tar industry has done to them. The struggle of artificial and natural dyes is similar to the struggle between the electric light and the older sources of light."

Testing Department :

Besides the manufacture of its sample charts and directions for use the dyestuff industry tests here the applications of new products and the tests are made even through actual experiments with light, water, soap, fulling and every other conceivable way, of the fastness, that is, the resistance of its colour against every particular action of use. This is explained, as we hear, by a justified demand of the consumers. For, the dye-stuff industry has first of all to satisfy itself with properties of the products before it puts the consumers to fruitless experiments! Through constant contact with the demands of the market it gains, however, a rich store of experience. Only a few new products pass the crucial test, and of these only very few show a marked originality, while the cost of production is the final decisive factor. Therefore the activity in the field of research offers no correct measure for the magnitude of the technical success. However, with the progressive constructive development one succeeds more and more to improve the deficient dye-stuffs in the direction indicated by the consumer through the introduction of the atom-groups known to be the carrier of the missing properties.

Factory Library and Reading Room :

We then follow the director of the laboratory to the reading room of the factory. No explanation is here necessary to attest to the influence of scientific and technical literature on the development and ceaseless vitalisation of the dye-stuff industry. Besides the patents, we find in the first row the Reports of the German Chemical Society, founded by Hofmann. These are the swift messengers, which carry the news of every new progress to the workshops of the industry. How inspiring indeed was the earliest messages of the *Berichte !* Liebig's great prophecy has proved true to the letters! From coal-tar the splendid dye-stuff of the madder plant has been derived! " If the factory

chemist won't read the *Berichte* any more "—says the laboratory director, " then he identifies himself with the old practitioners and soon he will be outflanked by the younger generation.   It should, therefore, be always borne in mind that new books and current periodicals are the life-blood of a progressive society."

Action of Light on Dyes :

The laboratory director then takes out a splendid collection of coloured photographs from one of the cupboards and explains to us that these most surprising although technically not yet utilized products of the coal-tar industry had been obtained as a result of the two contrary ways.   For, while the effect of light destroys the colour-tone in one direction, it creates it in the other.   To the typical diazo-process of Green, Cross and Bevan (*D.R.P.* 1890 *No.* 56606; *J. Soc. Chem. Ind.* 1890, 1001) belongs to the diazo-compound of Primuline, the light-sensitive substance.   At the points not touched by light a passage through solutions of β-naphthol, α-naphthylamine or other components, develops the corresponding wash-fast " Ingrain Colour."   In the second method of Feer (*D.R.P.* 1889, *No.* 53455; *Bull Soc. Ind. Mulh. 11th September,* 1889) the light sensitive layer consists of a mixture of β-naphthol sodium, or analogous phenol or amino components with the still ineffective diazosulphonates of toluidine, cumidine or tolidine.   Under the influence of direct sunlight the reactive diazo-compound is regenerated and simultaneously its coupling into insoluble orange, red or violet azo-dyestuff occurs.

He then presents us with a colourless substance impregnated ·with Feer's mixture.   We step to the window.   And how strange! Light the destroyer of colour at once produces an intensive illuminating red.

Closing Scene :

Then listen! a shrill, long-drawn signal sounds from the boiler house in front of us.   The steam whistle resounds.   It announces the close of the factory.   The call spreads.   From the farthest distance it echoes back, the voices mix to a roaring

accord. We look downwards. Life is come back. From all workshops it presses forth—first in pairs, then in hundreds. From all streets and lanes a thousand-headed merry coloured crowd roll slowly forward towards the outlet.

We bid farewell. "You must come again—often you must," says the director of the laboratory—"Every part of our industry stimulates contemplation, every investigator will lead you through his particular province of research—to-day you have listened to a foreword only."

We follow the guide to the factory gate. One last look to the organisation of the majestic work—its true factory secret becomes apparent to us!

Before our mind's eye stands again the tree of the German Chemical industry with its spreading branches and twigs. In what a natural way we reflect—has its powerful growth consummated. In science it had found its soil and nourishment and the rule of the eternal laws which are the foundations for every success in life has also brought the development to its present blossoming time. The wish emerges from the heart: May the storm never deprive it of the leaves and discord never gnaw at its marrow!

We make this remark to the guide. He shakes us by the hand. "Whenever you will remember this tree"—he says, "Don't forget the faithful gardener, who has nursed our tender plant ever since it was but a mere twig—almost half a century ago. Always remember in love and reverence our August Wilhelm von Hofmann!

Good bye!"

APPENDIX I

A Brief Account of the Synthetic Dyestuffs Discovered since 1892

In 1893 the first Sulphur Black was discovered by Vidal. The method consisted in preparing sulphur dyes by heating aromatic bases with sodium polysulphide. In 1899 formaldehyde came to be a new reagent for the production of New Magenta and later it also found application in the synthesis of Acridine dyestuffs.

In 1897 the *Badische Anilin und Sodafabrik* brought industrial synthesis of Indigo to successful completion. In 1902 the second commercial synthesis of Indigo was crowned with success by *Meister, Lucius and Brüning* Company.

In 1901, Indanthrene, the first member of very fast vat dyes was discovered. From anthraquinone several vat dyes of Indanthrene and Algol groups were prepared. Amongst vat dyes Dibenzanthrene, discovered by Bally in 1904, and Thioindigo by Friedländer in 1906, deserve special mention. In 1903 Cyanines, used as photographic sensitizer, first met with commercial success. By the thionation of Carbazole-indophenol a fast vat dye 'Hydron Blue' was discovered in 1909.

The trypanocidal agent Trypaflavine, an acridine dyestuff came to the market in 1910-1912.

During the World War I the progress was generally retarded. However, a series of 'self-mordanting' azodyes "The Neolan Colours" were discovered and to dye Viscose Silk special types of azodyestuffs the "Icyl Colours" developed.

Up to the year 1913 Germany covered about 75 per cent. of the total world production including about 90 per cent. of the synthetic dyestuffs used in Great Britain. But after the war a great change took place. In 1919 Britain began to meet 80 per cent. of her home demand by indigenous production.

The credit of the first complete commercial synthesis of anthraquinone vat-dye to be made outside Germany is due to Dr. J. Thomas of the Solway Dyes Company. In 1915 this British firm prepared Indanthrene from sodium anthraquinone- β -sulphonate. The United States independently produced these dyes in summer 1919. A glimpse into the dyestuff position of the U.S.A. may be had from a few lines of the 'Du Pont Research' written recently by E. F. Bolton, quoted below :

"In 1916 the Du Pont Company decided to enter the manufacture of dyes. The United States was almost wholly dependent upon German dyes at the outbreak of the World War I. When the British blockade was imposed, employment of millions of American workmen in the dye consuming industries was threatened. To make a rapid progress an agreement was made with the British firm Levinstein, Limited, which manufac-

tured a few intermediates and dyes prior to the war. After the outbreak of war Levinstein operated a former German-owned indigo plant which was modern in construction. This arrangement was very helpful, particularly in enabling the company to avoid the long time that would have been necessary for the development of an indigo process.

In starting the dye business, Du Pont was confronted by two serious difficulties :

> (i) The number of chemists with graduate training in research work was very small :

> (ii) The German patents licensed from the Chemical Foundation disclosed inadequate information and in many cases made no reference to the preferred methods of manufacture of the products covered by the patents.

Du Pont started the development of its dye business on a broad scale in the early twenties. From the beginning it was recognized that the manufacture of dyes could serve as the backbone of a synthetic organic chemical industry. To-day its Organic Chemicals Department, in addition to intermediates and dyes, is making rubber chemicals, petroleum chemicals, tetraethyl lead, synthetic camphor, detergents, wetting agents, seed disinfectants, perfume bases, photographic chemicals, neoprene and many other organic chemicals on huge scale."

After the World War 1 two big dyestuff combines were formed—one German and the other British. The German combine, the *Interessen Gemeinschaft für Farbenindustrie* was formed in 1924 by the amalgamation of almost all the well-known dye firms of Germany and in the same way by amalgamating all the British dye houses—"The Imperial Chemical Industries Limited " came into existence in 1926.

Recently the British Intelligence Objectives Sub-Committee has published a bulky report on " The Development of New Dyes and Colour Application Processes in Germany & Italy during World War II." The report states that a total of over one hundred new dyes plus many new intermediates have developed during the war years 1939-1945. Of the new organic chemicals for dye-synthesis cyclo-octatetrene formed by the polymerization of acetylene deserves mention. In this report it is also stated that the German manufacturing plants are far behind those in America from an engineering and operating point of view ; and as to research on new dyes, the I. G. technical men are very capable, but certainly are not superior to the Americans engaged in similar work.

Though the actual industrial position of Russia is not clear to us yet it may be safely assumed that her development in this direction is not of an ordinary order.

May we not hope that in near future India too will be in a position to meet the internal demand of dyestuffs ?

A few Dyestuff Intermediates with their Commercial Names

Commercial Name	Chemicals Name
Alizarine	.. 1, 2-Dihydroxyanthraquinone
Amino-G acid	.. 2-Naphthylamine-6, 8-disulphonic acid
Amino-R acid	.. 2-Naphthylamine-3, 6-disulphonic acid
Andresen's acid	.. 1-Naphthol-3, 8-disulphonic acid
Anisidine	.. o-Aminophenol methyl ether
Anthrachrysone	.. 1, 3, 5, 7-Tetrahydroxyanthraquinone
Anthraflavic acid	.. 2, 6-Dihydroxyanthraquinone
Anthranilic acid	.. o-Aminobenzoic acid·
Anthrarufine	.. 1, 5-Dihydroxyanthraquinone
Armstrong's acid	.. Naphthalene-1, 5-disulphonic acid
Badische acid	.. 2-Naphthylamine-8-sulphonic acid
Bayer's acid	.. 2-Naphthol-8-sulphonic acid
Benzidine	.. p. p′-Diamino-diphenyl
Brönner's acid	.. 2-Naphthylamine-6-sulphonic acid
Beta acid	.. Anthraquinone-2-sulphonic acid
Chromotrope acid	.. 1, 8-Dihydroxy naphthalene-3, 6-disulphonic acid.
Chrysazine	.. 1, 8-Dihydroxyanthraquinone
Cleve's acids	.. 1-Naphthylamine-6-and-7 sulphonic acid. (There are four other Cleve's acids).
Cresotic acids	.. Cresol carboxylic acids
Croceine acid	.. 2-Naphthol-8-sulphonic acid
Dahl's acid	.. 2-Naphthylamine-5-sulphonic acid
Disulpho acid S	.. 1-Naphthylomine-4, 8-disulphonic acid
DTS	.. Dehydrothio-p-toluidine sulphonic acid.
Delta acid	.. {1-Naphthol-4, 8-disulphonic acid / 1-Naphthylamine-4, 8-disulphonic acid
Ebert and Merz's acid	.. Naphthalene-2, 7-disulphonic acid
Epsilon acid	.. {1-Naphthol-3, 8-disulphonic acid / 1-Naphthylamine-3, 8-disulphonic acid
F acid	.. 2-Naphthol-7-sulphonic acid
Freund's acid	.. 1-Naphthylamine-3, 6-disulphonic acid·
G acid	.. 2-Naphthol-6, 8-disulphonic acid
Gallic acid	.. 3, 4, 5-Trihydroxybenzoic acid
Gamma acid	.. 2-Amino-8-naphthol-6 sulphonic acid
H acid	.. 1-Amino-8-naphthol-3, acid.
Histazarine	.. 2, 3-Dihydroxanthraquinone
Isoanthraflavic acid	.. 2, 7-Dihydroxyanthraquinone
J acid	.. 2-Amino-5-naphthol-7-sulphonic acid
K acid	.. 1-Amino-8-naphthol-4, 6-disulphonic acid.
Kalle's acid	.. 1-Naphthylamine-2, 7-disulphonic acid·
Ketone base	.. Tetramethyldiaminobenzophenone

Koch's acid	..	1-Naphthylamine-3, 6, 8-trisulphonic acid.
L acid		1-Naphthol-5-sulphonic acid
Laurent's acid	..	1-Naphthylamine-5-sulphonic acid
Lepidine	..	4-Methylquinoline
Leucotrope	..	Phenyldimethylbenzylammonium chloride.
M acid	..	1-Amino-5-naphthol-7-sulphonic acid
Mesidine	.	2, 4, 6-Trimethylaniline
Metanilic acid	...	Aniline-m-sulphonic acid
Michler's Ketone	..	Tetramethyldiaminobenzophenone
Naphthazarine	..	5, 6-Dihydroxy-1, 4-naphthoquinone
Naphthionic acid	..	1-Naphthylamine-4-sulphonic acid
o-Naphthionic acid	..	1-Naphthylamine-2-sulphonic acid
Naphthol A.S.	..	Anilide of hydroxynaphthoic acid
Naphthoresorcin	..	1, 3-Dihydroxynaphthalene
Nevile and Winther's acid	.	1-Naphthol-4-sulphonic acid
Nigrotic acid	..	1, 7, 3, 6-Dihydroxysulphonaphthoic acid
Nitroso base	..	p-Nitrosodimethylaniline
Peri acid	..	1-Naphthylamine-8-sulphonic acid
p-Phenetidine	..	p-Aminophenol ethyl ether
Phenyl-gamma acid	..	2-Phenylamino-8-naphthol-6-sulphonic acid
Phenyl Peri acid	..	Phenyl-1-naphthylamine-8-sulphonic acid.
Phosgene	..	Carbonyl chloride
Phthalic acid	..	o-Benzenedicarboxylic acid
Picramic acid	..	2-Amino-4, 6-dinitrophenol
Primuline base	..	p-Toluidine heated with sulphur
Purpurine	..	1, 2, 4-Trihydroxyanthraquinone
Pyrogallol	..	1, 2, 3-Trihydroxy benzene
Quinaldine	..	2-Methylquinoline
Quinizarine	..	1, 4-Dihydroxyanthraquinone
R acid	..	2-Naphthol-3, 6-disulphonic acid
2 R acid	..	2-Amino-8-naphthol-3, 6-disulphonic acid.
Red acid	..	1, 5-Dihydroxy naphthalene-3, 7-disulphonic acid.
Resorcinol	..	1, 3-Dihydroxybenzene
S acid	..	1-Amino-8-naphthol-4-sulphonic acid
Salicylic acid	..	o-Hydroxybenzoic acid
Schäffer's acid	..	2-Naphthol-6-sulphonic acid
Sulphanilic acid	..	Aniline-p-sulphonic acid
Thiocarbanilide	..	Diphenylthiourea
Tobias acid	..	2-Naphthylamine-1-sulphonic acid
Tolidine	..	Di-para-aminoditolyl
Toluidine	..	Amino toluene
Xylidine	..	Amino xylene
Yellow acid	..	1, 3-Dihydroxynaphthalene-5, 7-disulphonic acid

Well known Dyes with their Components

Dyes	*Components*
Acid Alizarine Blue B (acid dye)	Anthrarufine
Alizarine (vat dye)	Anthraquinone- β sulphonic acid
Aniline Blue (basic dye)	Aniline, Rosaniline base (from magenta).
Anthraquinone Vat Blue	2-Aminoanthraquinone (2 mols)
Anthraquinone Vat Yellow	2-Methylanthraquinone (2 mols)
Auramine O (basic dye)	Dimethyl aniline, phosgene
Bismarck Brown 2R (basic dye)	m-Toluylene diamine. (3 mols)
Chrysoidine Y (basic dye)	Aniline, m-phenylenediamine
Congo Red (acid dye)	Benzidine, sodium naphthionate
Direct Fast Yellow	p-Toluidine (4 mols), Sulphur
Eosine (acid dye)	Phthalic anhydride, Resorcin (2 mols)
Fast Black B (sulphur dye)	1, 8-Dinitronaphthalene and Sulphur
Gallocyanine (basic dye)	Nitrosodimethylaniline, gallic acid
Indanthrene Blue R (vat dye)	β -Aminoanthraquinone
Indigo (vat dye)	Aniline (2 mols), Chloracetic acid (2 mols)
Induline (spirit soluble)	Aniline, Aniline hydrochloride
Malachite Green (basic dye)	Dimethylaniline, benzaldehyde
Meldola's Blue (basic dye)	Nitrosodimethylaniline, β -naphthol
Metanil Yellow (acid dye)	Metanilic acid, diphenylamine ..
Methylene Blue (basic dye)	Dimethylaniline (2 mols), sodium thiosulphate.
Methyl Orange (acid dye)	Sulphanilic acid, dimethylaniline
Methyl Violet (basic dye)	Dimethylaniline (3 mols)
Naphthol Blue Black (acid dye)	p-Nitroaniline, H acid
Naphthol Black B (acid dye)	Amino-G-salt, R-Acid, alpha naphthylamine
Naphthol Green (acid dye)	Schäffer's acid
Nigrosine (acid dye)	Aniline, nitrobenzene
Orange II (acid dye)	Sulphanilic acid, β -naphthol
Patent Blue (acid dye)	m-Hydroxybenzaldehyde, diethylaniline
Phenolphthalein (indicator)	Phthalic anhydride, phenol (2 mols)
Pinacyanol	Quinaldinium salts, formaldehyde
Primuline (acid dye)	p-Toluidine, sulphur
Rhodamine B.	Diethyl-m-aminophenol, phthalic anhydride.
Rose Bengal G.	Dichlorophthalic anhydride, Resorcin
Safranine (basic dye)	Aniline, o-toluidine
Sudan I (spirit soluble)	Aniline, β -naphthol
Sulphur Black (sulphur dye)	2, 4-Dinitrophenol, sulphur
Tartrazine (acid dye)	Phenylhydrazine-p-sulphonic acid, dioxytartaric acid
Thioindigo Red (vat dye)	Thiosalicylic acid, chloracetic acid.
Vidal Black (sulphur dye)	p-Aminophenol sulphur

CHEMICAL CLASSIFICATION OF COAL-TAR DYES

Class	*Members*
Nitroso dyestuffs	.. Resorcin Green, Naphthol Green B.
Nitro dyestuffs	.. Picric acid, Martius Yellow, Naphthol Yellow S.
Azo-dyes—	
(*a*) Mono-azo	.. Para Red, Chloramine Blue 2B, Bismarck Brown, Aniline Yellow, Chrysoidine, Resorcin Yellow, etc.
(*b*) Poly-azo (bisazo, trisazo etc.)	Biebrich Scarlet, Naphthol Black, Congo Red, Columbia Black R, Diamine Green G etc.
Acridine and Quinoline dyes	. Benzoflavine, Acridine Yellow, Acridine Orange, Quinoline. Yellow and Cyanine.
Stilbene dyes	.. Mikado Yellow, Sun Yellow.
Thiazole dyes	.. Primuline, Thioflavine S.
Pyrazolone dyes	.. Tartrazine, Fast light yellow 2 G. Polar yellow 5 G, Eriochrome Red B.
Di- and Triphenylmethane dyes	.. Auramine, Magenta, Victoria Blue R.
Xanthene dyestuffs	.. Uramine, Eosine, Galleine, Rhodamine, etc.
Indamine and Indophenol dyes	.. Phenylene Blue, Bindschedler Green, Toluylene Blue, Indophenol Blue, etc.
Oxazine dyes	.. Gallocyanine, Meldola's Blue.
Azine dyes	.. Eurhodines, Safranines, Aposafranines Induline.
Hydroxyketone dyestuffs	. Alizarine, Flavopurpurine, Alizarine Yellow A, Anthracene Brown Alizarine Carmine, Alizarine Viridine, Alizarine Saphirol, etc.
Sulphide dyestuffs	.. Vidal Black, Fast Black B.
Vat Dyes	.. (a) Tyrian Purple, Ciba Green, Thioindigo Red, Indigo. (b) Anthraflavine G, Indanthrene Blue, Algol Blue. (c) Hydron Blue R.

Principal Characteristics of each Class

Nitroso- and Nitro-Dyestuffs—These are mostly yellow or brown in colour. On heating they decompose readily. When one or more hydroxyl groups are introduced into the molecule of an aromatic nitroso- derivative a good mordant dye is obtained.

Azo-Dyes (Mono- and Poly-azo dyes):—

About 70% of the coal-tar dyes belong to this group. Primary aryl-amines under certain conditions react with nitrous acid giving rise to the so-called diazonium compounds or diazonium salts which react readily with tertiary arylamines or phenols (not with aromatic hydrocarbons or halogen derivatives) yielding azo-compounds. Such derivatives are usually pleasantly coloured and possess basic or acidic properties and are known as azo-dyes. The group -N=N- is called the azo-group. According to the number of such groups in a dye-molecule it is called mono-azo, bis-azo or dis-azo, tris-azo, etc.

About the nature of the diazonium compounds : Nearly all diazo-nium compounds are extremely unstable and are fairly safe when damp or in solution. Large quantities of diazonium salts have to be handled carefully because their decomposition with water may increase to explosive violence if the heat of reaction is not removed. The diazonium salts of nitro-compounds are relatively stable. The beauty of the tone of the azo-dyes depends greatly on the care with which a large excess of nitrous acid is avoided.

There are three types of mono-azo dyes :—Benzene-azo-Benzene, Benzene-azo-Naphthalene, and Naphthalene-azo-Naphthalene dyestuffs.

Dis-azo dyes are mainly of the following types :—

(i) *Primary dis-azo dyes* are formed by the action of two diazo-compounds on a single arylamine or naphthol.

(ii) *Secondary dis-azo dyes* are produced by diazotizing an azo-dye containing a free amino group and coupling the newly formed diazo-compound with an arylamine or phenol.

(iii) Dis-azo dyes produced from arylamines such as benzidine, *o*-toluidine, *p*-phenylenediamine, etc. Many important substantive cotton dyes belong to this group.

Azo-dyes of the naphthalene series are of greater importance than those of the benzene series. Generally azo-dyes are formed in solution and are salted out, filtered, dried and powdered. Insoluble dyes are often generated on the fabric. Para Red may be cited as an example. Cotton fabric to be dyed is first steeped in a solution of sodium β-naphthoxide. It is then taken out, dried and immersed in 1% solution of *p*-nitrobenzene-diazonium chloride when the fabric is dyed red. Such dyes are known as 'ingrain' colours.

Acridine and Quinoline dyes :

In acridine dyes the acridine ring with its orthoquinonoid structure forms the chromogen. (When certain characteristic groups, 'Chromo-phores', such as, -N=N-, NO₂, etc. are present, the compound is coloured

12

or is a Chromogene ; and when, in addition to the chromophore, a strongly basic (*e.g.* NH₂) or acid group (*e.g.* OH or SO₂OH) is also present a dye is obtained).

Acridine is a coal-tar constituent but its derivatives are mostly synthesized. The amino, methylamino or arylamino derivatives of acridine show marked colour effect and Phosphine one of the oldest artificial dye-stuffs belongs to this group. With titanium mordants most of the acridine dyes are used in leather dyeing, imparting a fast yellow or orange shade. Some N-alkyl derivatives, *e.g.* Trypaflavine possess powerful disinfectant properties. Strong blue fluorescence is the choracteristic of all acridine dyes.

Quinoline dyes : Except 'Quinoline Yellow the members of this group of dyes are of no use to textile dyeing. But they are prized for their capacity to sensitize photographic plates,—the most important being Pinaverdol, Pinacyanol (Sensitol Red) and Dicyanine. The quinoline dyes are mostly red, pink or blue.

Stilbene dyes : The stilbene dyes are prepared from *p*-nitrotoluene and its derivatives. In addition to the stilbene group these dyes contain an azoxy or a nitroso group. Many stilbene dyes contain an azo-group. All stilbene dyes dye cotton from an alkaline bath leaving wool and silk uncoloured—a useful property for dyeing piece goods.

Thiazole dyes : They are derivatives of thiazole—Dehydrothiotoluidine and Primuline being the most important members of this group. They are yellow in colour showing strong blue fluorescence in alcoholic solution. Thioflavine T is a basic dyestuff used in calico-printing. It gives a greenish yellow shade.

Pyrazolone dyes : They are practically azo-dyes containing pyrazolone rings. Generally they impart yellow shades of great fastness on wool. Tartrazine is the most important and oldest dye of this group.

Di-and Triphenylmethane dyes : Auramine O, the ketoneimide, is the only important dyestuff of the diphenylmethane series. It is now generally prepared by fusing tetramethyldiaminodiphenylmethane with sulphur, ammonium chloride, and common salt, whilst ammonia is passed through the mass. Auramine G is the corresponding dye obtained from *o*-toluidine.

Triphenylmethane dyes : Though not very fast, the members of this group possess most brilliant shades of colour.

The triphenylmethane dyes are divided into the following main sub-groups :

(1) Derivatives of diamino-triphenylmethane (Malachite Green group).
(2) Derivatives of triamino-triphenylmethane (Rosaniline group).
(3) Derivatives of trihydroxy-triphenylmethane (Aurine group).
(4) Derivatives of triphenylmethane carboxylic acid (Eosine group).

The following are the important methods of preparation of this class of dyes :

A. The oxidation of para-arylamines (*e.g.* para-toluidine) and aromatic bases, the para positions of which are free, by means of oxidizing agents like nitrobenzene and arsenic acid.

B. The oxidation of an arylamine with *p*-*p*′-diaminodiphenylmethane or its derivatives.

C. The condensation of aromatic aldehydes with two molecules of an aromatic base—the condensing agent being zinc chloride.

D. Phosgene Process : The condensation of benzophenone derivatives with aromatic bases. The former are derived by the action of phosgene (carbonyl chloride) on dialkylarylamines.

E. The condensation of tetraalkyl-diaminobenzhydrol and its analogues with arylbases, phenols and their sulphonic acids.

These dyes when reduced with zinc and hydrochloric acid, stannous chloride or ammonium sulphide form leuco or colourless compounds. The leuco-compounds when oxidized (in air or with lead peroxide) they are converted back into the dyes.

Xanthene dyes : These dyes may be regarded as derivatives of diphenylmethane oxide or xanthene. They fall into two main groups—
   The Pyronines (derivatives of diphenylmethane).
   ' The Phthaleins (derivatives of triphenylmethane).
They may also be divided into :
      (*a*) Aminoderivatives.
      (*b*) Hydroxyderivatives.
The well-known groups of dyes, as Pyronines, Succineins, Rosamines and Rhodamines belong to the amino derivatives while Phthaleins belong to the Hydroxyderivatives.

Indamine and Indophenol dyes : The indophenol and indamine dyestuffs are derivatives of phenylated para-quinone mono and diimides respectively.

Indamines : Phenylene Blue obtained by oxidizing a mixture of aniline and paraphenylenediamine. The indophenols are produced by oxidising a mixture of a phenol (or naphthol) with a para-diamine or para-nitrosodimethylaniline.

Oxazine dyes : Oxazine grouping has got similar properties to the azine grouping. With mild reducing agents it is reduced to the leuco-compound. Most of the basic dyes of this group dye acetate-silk (Celanese) easily from an acid bath in the form of free bases. Oxazine dyes are used in cotton, silk and wool dyeing but in conjunction with Vesuvine and Chrysoidine some of these dyes, such as Meldola's Blue, find extensive use in leather dyeing. The first oxazine dyestuff to be manufactured was Meldola's Blue, obtained by condensing β-naphthol with an alcoholic solution of paranitrosodimethylaniline. Delphin Blue, Alizarine Green G, etc. belong to this group and are mordant dyes, being used in the same manner as Alizarine.

Azine dyes : These are basic dyes and are used in the form of salts. They are readily reduced to leuco-compounds with hydrosulphite, zinc dust and water, etc. and are easily re-oxidized in air. The azine-group occurs in different dyestuffs, such as Benzene-azines, Benzene-naphthaleneazines, Naphthalene-azines and Anthraquinone-azines. The latter belong to the Vat-dyestuffs. Azines are the longest known artificial dyes. Perkin's Mauve (Mauveine), the first artificial dyestuff belongs to the group of arylphenoazine. The azines are fugitive but beautiful colouring matters and they are being replaced by cheap azodyes. Nevertheless, Safranine, Indoine, Indulines and Nigrosines

are still holding the ground. Wool Fast Blues and Indulines are very fast dyes. Aniline Black (ingrain colour) is an important member of the Azine dyes.

Hydroxy-Ketone dyes : They are all mordant dyes. Hydroxynaphthaquinone dyes, such as Naphthazarine, have lost their importance and have been replaced by Eriochrome Black T, Galloflavine W, which are used to a great extent in calico-printing.

Hydroxy-Ketone dyes are all hydroxylic compounds hence acidic in nature and contain two hydroxyl groups in the ortho-positions. They produce lakes with oxides of aluminium, chromium, iron, tin, etc. The colour produced depends on the constitution of the dye as well as on the mordant used. A number of sulphonic acids obtained by heating the dyes of this group with fuming sulphuric acid are known. Anthraquinone dyes fall into three main sub-groups :

(*a*) Mordant-dyeing Anthraquinone dyes, (*b*) Anthraquinone Acid dyes, (*c*) Anthraquinone Vat dyes.

Sulphide dyes : These dyes are of complex constitution probably containing a thiazine ring. They are insoluble in water but soluble in sodium sulphide solution, from a bath of which they are applied to cotton fabric and then oxidized in air or treated with a metallic salt.

Vat dyes : They are a group of insoluble dyestuffs which are reduced to alkali-soluble leuco-compounds. The fabric is treated with the leuco-compound and is oxidized by atmospheric oxygen to the dyestuff on the fibre. They all contain $=CO$ or $=CS$ group in their molecule which is converted into $=CHOH$ or $=CHSH$ on reduction.

CLASSIFICATION OF DYES WITH RELATION TO TEXTILE FIBRES

Acid Dyes : Acid dyes are the sodium salts of sulphonic acids as well as dyes containing phenolic groups associated with nitro groups. They are so called because of their acid character as well as their application to wool from an acid bath. *They are substantive to wool* upon which they are fixed from a bath acidified with dilute sulphuric or acetic acid. The acid dyes are mainly used in wool and silk dyeing and rarely in cotton dyeing. They do not form lakes with tannin. According to their chemical composition they fall into the following categories :
(1) Those containing nitro-groups, (2) Those containing sulphonic acid group, and (3) Those which are azodyes.

Basic Dyes : Basic dyes belong to the group of substituted amines. They are mostly salts of colour bases consisting of aromatic amines and substituted amino-compounds with zinc chloride or hydrochloric acid. They possess direct affinity for wool and silk which are dyed from an acid bath of dilute sulphuric, acetic or tartaric acid. But *they are mainly used for dyeing cotton fibre on a tannin mordant.* The basic dyes are generally non-fast dyes and seldom used for dyeing animal fibre. They can, however, be applied to jute directly. Cotton fabric which has already been dyed with some other classes of dyes is some-

times "topped" with a basic dye to brighten the shade. Cellulose acetate rayon is also dyed with basic dyes. Basic dyes are also used· in dyeing viscose and cellulose nitrate rayons.

Direct or substantive cotton dyes (salt colours) : The dyes which are absorbed directly from their solution by the fibre and require no help of a mordant are called substantive cotton dyes. Cellulose Rayon and Cotton are dyed directly from a neutral bath in which some sodium sulphate is present. Basic dyes are generally more brilliant and mordant dyes much faster than the substantive cotton dyes. Congo Red is the oldest member of this group of dyes which are characterized by their ready solubility in water. Benzopurpurine, Chrysamine, Azoblue, D'anol brilliant red, Diamine blue 2B, Cotton yellow G, Benzo violet R, et·., also belong to this group. Some substantive dyes are applicable to wool also.

Mordants and Mordant or Adjective Dyes : Mordants are substances capable of combining with certain coloured compounds to form insoluble coloured compounds (lakes) which by certain operations may be permanently fixed upon the textile materials. There are metallic, non-metallic and acid mordants. Metallic mordants usually comprise of metallic oxides, hydroxides or extremely basic salts which can combine with certain dyes to form insoluble coloured compounds. Sulphur is the only non-metallic mordant of importance. To notable acid mordants belong tannic acid and various fatty acids, such as, oleic acid, stearic acid, and Turkey-red oil. (Turkey-red oil, sodium sulphoricinoleate) is prepared from castor oil by sulphuric acid at a low temperature. The free mineral acid is removed by washing—the unchanged oil by ether and the generated sulphoricinoleic ·acid is neutralized with sodium hydroxide. It is a jelly-like transparent liquid. It is used in the leather and textile industries). Acid mordants are used with basic mordant-dyes for application on cotton fabric.

True mordant dyes are those colouring substances which form metallic dye lakes directly (without preliminary oxidation). The lakes of specific dyes with different metals often vary in colour tone very considerably. Alizarine may be cited as an example. Aluminium, chromium and iron lakes of Alizarine are red, maroon and violet respectively. But this is not true for all the mordant dyes. Mordant dyes cannot be permanently fixed upon cotton, wool or silk except in conjunction with some mordant.

Mordant Acid dyes are intermediate in general character between the Acid dyestuffs and the mordant dyestuffs. They resemble acid dyes in dyeing wool directly in an acid bath but at the same time resemble mordant dyes in that they may be applied to advantage in conjunction with metallic mordants.

Vat Dyes : Vat dyes are a class of compounds insoluble in water but when reduced with sodium hydrosulphite or other suitable reducing agents they are converted into "leuco" compounds soluble in dilute alkali and in this state they are adsorbed by the fibre. When the fabric impregnated with the leuco-compound is taken out of the dye bath and exposed to the air the leuco-compound is converted into the insoluble dyestuff by aerial oxidation and remains fixed in the fibre. Vat dyes

are distinguished by their remarkable fastness. The word vat-dye is derived from the age-long practice of the dyers in their conducting the process of dyeing (particularly, in their application of the natural Inligo) in vats. Vat dyes fall into three main sub-groups : (1) Indigoid vat dyes, (2) Anthraquinone vat dyes, and (3) Sulphurized vat dyes.

Ingrain Dyes : Ingrain dyes are those the final stage of production of which is carried out upon the fibre. The shades obtained by these dyes have great brilliance and fastness. These dyes are divided into three broad sub-groups : (1) Ice colour—these are produced by impregnating the fibre with the secondary component of an azo-dye, that is a phenolic compound and then developing the final colour by immersion in an ice cold bath of a diazonium-salt. (2) A direct cotton dye containing a free amino group is first applied to the fibre. It is then diazotized and developed by immersion in a bath of secondary component. (3) Aniline Black—this is the black formed by the oxidation of an aniline salt and is produced by oxidizing a fibre impregnated with an aniline salt or by heating the fibre with a solution of an aniline salt containing an oxidizing agent.

Sulphur Dyes : These dyes owe their name to the fact that sulphur or sodium sulphide is used in their manufacture, sulphur is one of their constituents and their dyebath also invariably contains sodium sulphide. These dyes are insoluble in water but soluble in sodium sulphide solution from which they are applied to cotton and are later oxidized in air or treated with a metallic salt. They are highly prized due to their fastness to light, washing and acid and are extensively used in dyeing cotton fabrics to which they impart black, blue and brown colour. Bright red colour is seldom obtained from sulphur dyes.

Pigments : Some of the coal-tar dyes are insoluble in water and are used for colouring of paints, lacquers, varnishes and printing ink. These are known as Pigment dyes.

True dyestuffs—are those which contain sulphonic or other groups which render them soluble in water.

Lake Pigments : A number of true dyestuffs contain in their molecule special groupings capable of combining with some metal or acid which renders them insoluble. The resulting insoluble dyestuffs are known as lake pigments. A number of lake pigments are used in printing ink. The lakes are prepared from acid dyestuffs from the solution of their sodium or potassium salts in which form they appear on the market by precipitating with barium chloride, stannous chloride, aluminium chloride, lead acetate, etc. These lakes are more resistant to sunlight than those produced from the basic dyestuffs, unless the latter have been precipitated with phosphotungstic or phosphomolybdic acids.

More about the Application of Dyestuffs

Textile colouring includes Dyeing and Printing.

The term *Dyeing* denotes processes in which entire body of the fabric to be coloured is immersed in the dye-bath.

Textile Printing is effected by means of a roller printing machine, blocks or screens to certain portions of the fabric, imparting to it a definite coloured design. The requisite dyestuffs and chemicals are made into a paste with starch, dextrine, etc., and applied to the fabric with the help of a machine. Multi-coloured prints are usually made. Pleasing effects are secured by the combination of dyeing and printing.

Staining is defined as the application of dyes on wood, bone and ivory with the help of a brush. It is generally a superficial application. A combination of staining and dyeing is met with in the colouring of leather, straw, paper and feathers. Staining of bacteria, etc., for microscopic examination is also a wellknown term. The selective adsorption of the dye by different kinds of cells is utilized here.

DYEING REQUISITES

Besides dyestuffs proper, a number of chemicals is generally employed in dyeing operations. They are :

(1) Mordants :   (*i*) Metallic, (*ii*) Non-metallic, (*iii*) Acid ;
(2) Mordanting Accessories ; (3) Chemical fixing agents ;
(4) Mechanical fixing agents ; (5) Developing agents ;
(6) Dyeing Accessories.

Mordants—The subject has just been discussed.

Mordanting accessories—These are substances generally possessing reducing properties. Tartar emetic, lactic and oxalic acids, residual products of sulphite pulp waste liquor and sulphuric acid belong to this class. When used in conjunction with mordanting principle they effect gradual decomposition of the latter giving rise to a uniform deposition of the actual mordant upon and within the treated textile fibre. By mordanting principle is meant the compound which produces the mordant. Thus the soluble sodium or potassium dichromate used in wool-mordanting processes is the *mordanting principle* but the insoluble chromium chromate and chromium hydrate fixed on the fibre constitute the *true mordant*.

Chemical fixing agents : Compounds of antimony used to fix the mordant tannic acid to the fibre belong to this group. Sometimes sodium carbonate acts as a fixer by precipitating basic carbonate and hydrate of iron upon the fibre when the latter had previously been immersed in a bath of the nitrate of iron.

Mechanical fixing agents : These include albumen, gums or starch capable of holding the dyestuff mechanically on the fibre for a certain length of time. When desired effect has been produced these agents are removed from the fibre by steaming or otherwise.

Developing agents : Ingrain colours offer such examples. Fabric drenched with an alkaline solution of β-naphthol when immersed in a solution of diazotized paranitroaniline, Para Red is formed on the fabric. Here the diazo-solution is the developing agent. Similarly when a fabric dyed yellow with Primuline is diazotized with a solution of nitrous acid and then immersed in a solution of β-naphthol the fabric assumes a bright red appearance. In this case β-naphthol is a developing agent.

Dyeing Accessories : Several types of compounds fall into this category.

Levelling agents are introduced into the dyebath to effect a level or even deposition of the dye on the fibre. Sodium sulphate which is used in conjunction with acid dyes in wool-dyeing constitutes a levelling agent.

Exhausting agents effect a greater adsorption of the dye by the fibre with consequent exhaustion of the dye in the dyebath. Sodium sulphate and sodium chloride used in the bath of direct cotton dyes belong to this class.

Penetrating agents facilitate proper penetration of dyes into the fibre. Mixture of sulphonated oils, soap and certain organic solvents are generally employed for the purpose. Recently a number of sulphonated higher alcohols and esters have come to be largely used as penetrating and wetting out agents.

OUTLINES OF PRACTICAL DYEING

Direct Dyeing : For direct dyeing of cotton it is necessary to prepare a dye-liquor containing a requisite amount of dyestuff and Glauber's salt, common salt or soda or a mixture of them. The method of working is to put a clean piece of cotton fabric in a lukewarm or even a hot bath, raise it to the boil, allow the fabric to remain in the boiling bath for half an hour to an hour, then take it out, wring, wash and dry. Strong boiling of the bath is not required—a gentle simmer gives the best results. Percentage of the dye and accessories needed vary with different dyes and it has to be found out by the dyer. Some hints may be had from practical treatises on the subject.

Mordant Dyeing : Dyeing with Eosine may serve as an illustration. For the production of Eosine pinks and scarlets on cotton the following operations are resorted to : (*a*) Impregnating the fabric with sodium stannate, (*b*) Fixing the oxide of tin with dilute sulphuric acid, and (*c*) Immersing the mordanted fabric in a bath of Eosine.

Clean piece of fabric is steeped in a bath of sodium stannate at 8° Tw and when thoroughly impregnated it is taken out and wrung. The fabric is then put in a bath of sulphuric acid at 2—4° Tw when sodium stannate is decomposed and deposited on the fibre as oxide of tin or stannic acid. The fabric is then taken out, washed with water and introduced into a bath of Eosine, the temperature of which is gradually raised to 180°F and maintained at that temperature till the desired shade of colour is obtained.

Vat Dyeing : Dyeing with Indigo is a common example. It consists in (*a*) The preparation of Indigo solution or "setting the dye vat", (*b*) Steeping the cotton fabric in the vat, and (*c*) Exposing the impregnated fabric to the air.
The following are the usual methods of "setting the dye vat" :
(*i*) With lime and copperas, (*ii*) Zinc and lime vat, and (*iii*) Zinc and sodium bisulphate.

A brief description of the zinc and lime vat is given below : In 1200 c.c. of water at 50°C, 100 grammes zinc dust added and stirred. To it 500 g. of Indigo (20% paste) followed by 300 g. unslaked lime are added and thoroughly agitated. It is then left to stand for 5-6 hours

with intermittent stirring. The reduced dye liquor shows a yellow colour. It is then diluted with 5 litres of water and cotton fabric is steeped in this solution, wrung out and dried. The process is repeated till the requisite blue shade has been imparted to the fabric.

It needs scarcely any mention that with the diversity in the nature of dyes, mordants and particularly of the fabrics, there is a wide variation in the process of dyeing. The above serves but a preliminary introduction to the vast subject of dyeing with its manifold complexities. For successful dyeing, besides the purity of the requisite dyes and chemicals, the quality of water used is also an important factor.

EXTRA-TEXTILE USE OF DYES·

Besides serving the major function, viz., the dyeing of textile fabrics, the coal-tar dyes find useful application, though to a limited scale, in a number of other spheres of civilized life, the most important of which are given below :

Food Colours : To this group belong generally—Naphthol Yellow, Aminoazobenzene, Aminoazotoluene, Ponceau 2R, Bismarck Brown, Tartrazine, Magenta, Guinea Green, Erythrosine and Indigo Carmine.

Soap Dyes : Methyl Violet, Alizarine, Naphthol compounds, Metanil compounds, Chrysoidine, Diazamine compounds, Paramine compounds, Rhodamine, Safranine, Bismarck Brown, etc.

Printing Ink Dyestuffs : Lakes and Pigments only are used here. The following deserve special mention : Alizarine lakes, Anthosine, Eosine, Phloxine, Rose Bengal, Acid Green, Malachite Green, Victoria Green, Hansa Yellow 3G, Persian Orange, Lithol Red, Lithol Rubine, Methyl Violet, Para Red, Peacock Blue, Permanent Orange, Pigment Scarlet, Tartrazine Yellow lake, Magenta, Rhodamine, Indanthrene, Methylene Blue, Quinoline Yellow, Naphthol Yellow S, Induline Blue, etc.

Writing Ink Dyes :

Red—Eosine, Erythrosine, Phloxine, Acid Fuchsine, Poncean Scarlet, Cotton Scarlet, etc.

Blue—Indigo Carmine, Soluble Blue, Methylene Blue, Benzol Blue, etc.

Violet—Acid Violet, Methyl Violet.

Green—Neptune Green, Light Green, Malachite Green, Brilliant Green.

Yellow—Fast Yellow, Tartrazine, Metanil Yellow, Acid Yellow.

Orange—Cotton Orange, Alkali Orange, Gold Orange.

Paper Dyes :

Acid colours used in sized papers in the beater—Metanil Yellow, Naphthol Yellow, Orange II, Croceine Scarlet, Fast Red A, Nigrosine, Ochre Buff.

Substantive dyes for paper dyeing—Dianol fast yellow, Vesuvine, Orange R, Congo Orange R, Congo Red, Congo Rubine, Dianol Fast Ped K.

Basic colours used both on sized and unsized pulps—Magenta brands, Phosphine brands, Chrysoidine, Bismarck Brown, Methylene Blue, Iodine blue brands.

Sulphide colours used—Thionol yellow G.R., Thionol Orange L, Thionol Green 3B.

Photographic Dyes :

Important dyes used as sensitizers—

The Phthaleins—of these Erythrosine and Eosine are widely used for rendering AgBr sensitive to yellow and green rays and consequently for the manufacture of " Orthochromatic " plates.

Monobromfluorescein is used as a green sensitizer for silver bromide.

Rosaniline dyes—Ethyl violet and Formyl Violet.

Azo dyes—Benzonitrol Brown, Dianil Black R, Glycine Red, Pluto Black, Alizarine Blue, Nigrosine D.

Quinoline Dyes—Pinaverdol, Pinacyanol (Sensitol red), Dicyanine, Pinachrom, Perikol.

Dyes for Colour filters—Auramine O, Tartrazine, Fast Red D, Chrysosulphite and Coxin.

Dyes for Colouring the gelatine—Auramine, Brilliant Green, Crystal.Violet, Fuchsine, Methylene Blue, Phenosafranine, Rhodamine, Acid Green, Congo Red, Naphthol Green, Filter Yellow, Patent Blue, Tartrazine, Rapid Filter Red, etc.

Leather Dyeing :

In respect of dyeing leather resembles wool consequently both acid and basic dyes are used specially on leather tanned with vegetable tannin material. On chrome-tanned leather some mordant dyes, basic and acid dyes as well as direct cotton dyes are used.

Dyes used as Indicators :

Thymol Blue, Bromphenol Blue, Congo Red, Methyl Orange, Bromcresol Green, Methyl Red, Chlorphenol Red, Alizarine Red, p-Nitrophenol, Bromcresolpurple, Bromthymol Blue, Phenol Red, Neutral Red, Cresol Red, Metacresol Purple, Thymol Blue, Phenolphthalein, Alizarine Yellow, Tropeolin O, etc.

DYESTUFF AS FORERUNNER OF CHEMOTHERAPY

Ehrlich had been the chief agent in the introduction of the use of synthetic dyestuffs into medical histology and had actually tried an experimental therapy of malaria with Methylene Blue as early as 1891.

The effective beginning of modern chemotherapy was made with the transmissible disease due to trypanosomes. Ehrlich found the benzidine dyestuff Trypan-Red as the first effective cure for such an infection in mice. Trypan Red, though now of historical interest only, has provided the starting point not only for all modern chemotherapy but for the particular line of advance, through Afridol-Violet which ultimately led to Germanin (Suramin), the most effective of the remedies for trypanosomiasis.

It is also of interest to remember that out of the consideration of the structures of quinine and Methylene Blue emerged atebrin, practically the fore-runner of the successful synthetic antimalarials.

Genesis of Sulphonamide : Almost from the very inception of the azo-dyes the search for their therapeutic use has been tried. Even in 1909 Hörlein working on azo textile dyes found that a particular azocompound possessed a limited therapeutic action against mouse septicemia

caused by haemolytic streptococci. Later Domagk discovered 2, 4-Diamino-azobenzene-4'-sulphonamide hydrochloride which was patented by Mietzsch and Klarer in 1935 under the name .of " prontosil I ".

Further search for a more soluble and less toxic compound led to the development of the disodium salt of 4'-sulphonamidophenyl-2-azo-7-acetylamino-1-hydroxynaphthalene-3, 6-disulphonic acid under the trade name of " prontosil II ". Success of these and other similar compounds attracted pointed attention of the workers to this field and as a result investigations of their mechanism of action and also to the search for ideal compounds ultimately revealed p-aminobenzenesulphonamide to be the active therapeutic agent and the azo linkage was proved not at all to be an essential factor. The subsequent history of the hosts of• highly potent sulphonamide derivatives of wide range of therapeutic activity is too vast a subject to be mentioned here.

Medicinal Dyestuffs : Bactericides and Antiseptics : Malachite Green, Brilliant Green, Methyl Violet, Gentian Violet, " Mercurochrome ". Acri-Violet or a mixture of Acriflavine and Gentian Violet is also an important item. Skin growth promoters (over wounds): Aminoazotoluene and its mono- and di-acetyl derivatives ; Biebrich Scarlet R. Med.

Those used in Protozoal Diseases : Trypan Red, Trypan Blue.

Methylene Blue is useful in the selective staining of nerve cells while Crystal Violet is used in the selective bacterial culture.